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Some cyclic organosilicon compounds and derivatives

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SOME CYCLIC ORGANOSILICON COMPOUNDS AND DERIVATIVES

by

Richard David Gorsich

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Major Subject: Organic Chemistry

Approved:

Signature was redacted for privacy.

In Charge of Major Work

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Iowa State College

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TABLE OF CONTENTS

	Page
INTRODUCTION	1
HISTORICAL	4
Preparation of Functional Cyclic Organosilanes	4
Preparation of Nonfunctional Cyclic Organosilicon Compounds	11
Properties of Cyclic Organosilicon Compounds	15
Chemical properties	15
Physical properties	22
EXPERIMENTAL	30
Tetraarylsilanes Containing a Halophenyl Group(s)	32
Reaction of <u>m</u> -fluorophenyllithium with carbon dioxide	33
Run 1	33
Run 2	33
Reaction of <u>m</u> -fluorophenylmagnesium bromide with carbon dioxide	34
Tetrakis-(<u>m</u> -fluorophenyl)-silane	35
Tetrakis-(<u>m</u> -fluorophenyl)-germane	36
Tris-(<u>m</u> -fluorophenyl)-phenylsilane	36
Bis-(<u>m</u> -fluorophenyl)-diphenylsilane	37
<u>m</u> -Fluorophenyltriphenylsilane	38
<u>n</u> -Dodecyltris-(<u>m</u> -fluorophenyl)-silane	38
Tris-(<u>m</u> -fluorophenyl)- <u>n</u> -hexadecylsilane	39
Tris-(<u>m</u> -fluorophenyl)- <u>n</u> -octadecylsilane	40
<u>m</u> -Chlorophenyltriphenylsilane	40
Bis-(<u>m</u> -chlorophenyl)-diphenylsilane	41
Tris-(<u>m</u> -chlorophenyl)-phenylsilane	42
Tetrakis-(<u>m</u> -chlorophenyl)-silane	42
Trialkylsilyl and Triarylsilyl Compounds	43
1,2-Ethylenebis-[tribenzylsilane]	43
1,2-Ethylenebis-[tri-2-ethylhexylsilane]	44
1,2-Ethylenebis-[tri- <u>n</u> -hexadecylsilane]	44
<u>m</u> -Phenylenebis-[tribenzylsilane]	45
<u>m</u> -Phenylenebis-[tri- <u>n</u> -decylsilane]	46

	Page
p-Phenylenebis-[tri-n-decylsilane]	47
4-Pentenyltriphenylsilane	48
1,5-Pentamethylenebis-[triphenylsilane]	49
Method A	49
Method B	49
3,3'-Biphenylenebis-[triphenylsilane]	50
Organosilylmethylolithium Compounds	51
(Chloromethyl)-methyldiphenylsilane (impure)	51
(Chloromethyl)-methyldibenzylsilane (impure)	52
(Chloromethyl)-di-n-tetradecylmethylsilane (attempted)	53
[(Methyldiphenylsilyl)-methyl]-diphenylmethanol	54
[(Methyldibenzylsilyl)-methyl]-diphenylmethanol	55
Metalation Reactions	56
Reaction of n-butyllithium with furan	56
Reaction of phenyllithium with dibenzothiophene	56
Reaction of lithium with cyclopentadiene	57
Run 1	57
Run 2	58
Reaction of lithium with fluorene	59
Reaction of lithium with 9-phenylfluorene	59
Preparation of 9,9-diphenylfluorene	60
Reaction of lithium with triphenylmethane (attempted)	61
Cleavage of a Carbon-Carbon Bond by Lithium	61
Reaction of lithium with 9,9-diphenylfluorene	61
Cleavage Reactions of Some Noncyclic Organosilicon Compounds	62
Preparation of diphenylsilane	62
Preparation of methyldiphenylsilane	63
Reaction of lithium with diphenylsilane	64
Reaction of lithium with tri-2-biphenylsilane	64
Reaction of lithium with methyldiphenylsilane	65

	Page
Run 1	65
Run 2	66
Reaction of lithium with triphenylsilane	67
Run 1	67
Run 2	69
Run 3	70
Run 4	71
Reaction of lithium with triphenylgermane	72
Run 1	72
Run 2	73
Reaction of lithium with tetraphenylsilane	74
Reaction of phenyllithium with triphenylsilane	74
Reaction of phenyllithium with triphenylgermane	75
Reaction of triphenylsilyllithium with triphenylsilane	75
Reflux temperature	75
Room temperature	76
Reaction of triphenylsilyllithium with refluxing tetrahydrofuran	77
Aromatic Heterocycles Containing Silicon as the Hetero Atom	79
2,2'-Biphenylenedilithium	79
5,5'-Spirobi-[dibenzosilole]	80
5,5'-Spirobi-[dibenzogermole]	80
5-Chloro-5-n-dodecyldibenzosilole	81
5,5-Dichlorodibenzosilole (impure)	82
Method A	82
Method B (attempted)	83
5-Benzyl-5-chlorodibenzosilole (impure)	84
5-Chloro-5-phenyldibenzosilole	85
5-Chloro-5-methyldibenzosilole (impure)	86
Reaction of 2,2'-biphenylenedilithium with hexachlorodisilane	87
<u>o</u> -Bromobenzyl bromide	88
2,2'-Dibromobibenzyl	88

10,11-Dihydro-5,5-diphenyldibenzosilepin	89
Spiro-[dibenzosilole-5,1'-silacyclohexane]	90
5,5-Diethyldibenzosilole	91
5,5-Di- <u>n</u> -dodecyldibenzosilole	92
5- <u>n</u> -Dodecyl-5-phenyldibenzosilole	93
5-(3-Biphenyl)-5- <u>n</u> -dodecyldibenzosilole	93
5- <u>n</u> -Dodecyl-5- <u>n</u> -hexadecyldibenzosilole	94
5,5-Di- <u>n</u> -tetradecyldibenzosilole	95
5- <u>n</u> -Dodecyl-5-[(methyldibenzylsilyl)-methyl]- dibenzosilole	95
5,5-Dimethyldibenzosilole	96
5-Benzoyldibenzosilole	97
5-Phenyldibenzosilole (impure)	97
5,5-Diphenyldibenzosilole	98
Method A	98
Method B	98
Method C	99
5,5'-Dimethyl-5,5'-bi-[dibenzosilole]	99
5,5'-Di- <u>n</u> -dodecyl-5,5'-bi-[dibenzosilole]	100
5,5'-Diphenyl-5,5'-bi-[dibenzosilole] (attempted)	101
5-Hydroxy-5-methyldibenzosilole (attempted)	101
5,5'-Oxybis-[5-methyldibenzosilole]	102
5,5'-Oxybis-[5- <u>n</u> -dodecyldibenzosilole]	103
Reaction of formic acid with 5,5- diphenyldibenzosilole	104
Reaction of 2,2'-biphenylenedilithium with 5-chloro-5-methyldibenzosilole	104
Reaction of 2,2'-biphenylenedilithium with triethylchlorosilane (attempted)	105
5-(2-Biphenyl)-5-phenyldibenzosilole	106
From 5,5'-spirobi-[dibenzosilole] and phenyllithium	106
From 5-chloro-5-phenyldibenzosilole and 2-biphenyllithium	106
Reaction of lithium with 5,5- dimethyldibenzosilole	107
Reaction of lithium with 5,5'-dimethyl- 5,5'-bi-[dibenzosilole]	108

	Page
DISCUSSION	109
Noncyclic Organosilicon Compounds	109
Organosilylmethylolithium Compounds	114
Metalation Reactions	116
Cleavage of a Carbon-Carbon Bond by Lithium	119
Cleavage Reactions of Some Noncyclic Organosilicon Compounds	119
Cyclic Organosilicon Compounds	132
Suggestions for Further Research	147
SUMMARY	149
ACKNOWLEDGMENT	152

INTRODUCTION

The excellent thermal stabilities and oxidative stabilities of certain organosilicon compounds were two factors influential in stimulating commercial interest in the development and production of some of these types which, even today, are considered custom chemicals. Prior to this industrial activity very little effort had been made to prepare and evaluate organosilicon compounds which might possess favorable thermal stabilities; though organic compounds of silicon have been the subject of numerous investigations during the past years. Even with the rapid rise of this new industry, emphasis has been concentrated primarily on polyorganosiloxanes, commonly referred to as silicones, because of their diverse applications, but mainly because economic and commercial considerations are more favorable to the large-scale adaptation of silicones than to monomeric organosilicon types. As a consequence, the potential of monomeric organosilicon compounds as thermally stable materials to be utilized at elevated temperatures has hardly been scrutinized either industrially or in university laboratories.

Accordingly, one of the purposes of this work was to synthesize some monomeric organosilicon compounds for possible use as high temperature lubricants and related applications. One part of this problem was essentially an extension of some

earlier studies¹ which dealt with an evaluation or qualitative comparison of the abilities of various organic moieties to impart thermal resistance to a molecule. The second part of this problem was concerned with finding a versatile nucleus to which some of the more promising organic groupings could be attached. The dibenzosilole ring system, an aromatic heterocycle with silicon as the hetero atom, was selected for this purpose since, in addition to being synthetically versatile, it also possessed aromatic character which was deemed important in minimizing oxidation and increasing radiation resistance of the molecule at elevated temperatures.

Another purpose of the investigation was to compare the chemical properties and physical properties of dibenzosilole types with both their open-chained analogs and with their carbon analogs. The chemical studies were limited to hydrolysis reactions, reduction reactions, and Wurtz-type coupling reactions of functional² dibenzosilole compounds, and to cleavage reactions of nonfunctional dibenzosilole types by

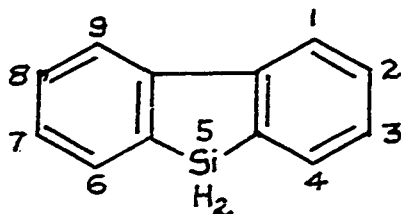
¹J. J. Goodman, Unpublished Ph.D. Thesis, Iowa State College Library, Ames, Iowa (1950).

²In this thesis functional will be used in a restricted sense to denote compounds containing a silicon-halogen bond(s), a silicon-hydrogen bond(s), and a silicon-alkoxy or -aryloxy bond(s). Nonfunctional cyclic types will include compounds containing only silicon-carbon bonds as well as derivatives having a silicon-hydroxyl bond(s), a silicon-silicon bond, and silicon-oxygen-silicon bonds.

lithium in tetrahydrofuran and in diethyl ether. Similar cleavage reactions of some open-chained compounds were reinvestigated to ascertain the mode of reaction as well as to compare them with the cleavages of their cyclic organosilicon counterparts.

Paralleling the systematic studies of organic radicals to be incorporated in the dibenzosilole nucleus was a related investigation aimed at improving known preparative procedures, especially with regard to finding new methods for introducing organic groupings into the dibenzosilole framework.

The nomenclature and numbering system for all cyclic organosilicon compounds are in accord with those used and recommended by Chemical Abstracts. The numbering of the dibenzosilole ring system is shown in the illustration (I).



I

HISTORICAL

In this review an attempt has been made to record all of the cyclic organosilicon compounds abstracted in Chemical Abstracts through December, 1955. The author index of Chemical Abstracts has been reviewed through April, 1957, and Current Chemical Papers have been thoroughly checked through April, 1957. The original and cross references were consulted whenever possible.

It has been the intent of this compilation to summarize the preparation and properties of silicon-containing ring systems in which silicon is bonded only to carbon. Accordingly, numerous polycyclic organosiloxanes and polycyclic organopolysilanes, as well as any other ring system containing a silicon atom bonded to a hetero atom, will be omitted.

The review has been arbitrarily divided into three main parts: first, preparations of functional cyclic organosilanes; second, preparations of nonfunctional cyclic organosilanes; third, properties of cyclic organosilanes.

Preparations of Functional Cyclic Organosilanes

The first mention of a cyclic organosilicon compound appeared in the literature in 1887 when Hart³ claimed he had

³W. B. Hart, Rev. Brit. Assoc., 661 (1887).

prepared 1,1-dichlorosilacyclohexane by a sodium condensation from one mole of 1,3-dibromopropane and one mole of silicon tetrachloride. There was considerable doubt about the assigned structure based on marginal elementary analyses and, indeed, the results could not be duplicated by Widdowson⁴ who recommended the compounds be deleted from the literature.

Hart's controversial investigation was actually the stimulus for the first successful preparation of a functional cyclic organosilicon compound. Prior to Widdowson's repetition of Hart's work, Bygden⁵ was also extremely dubious of the latter's results and, therefore, employed a different approach to the synthesis of a silicon-containing heterocycle. He introduced silicon into a six-membered ring by allowing one mole of 1,5-pentamethylenedimagnesium dibromide to interact with one mole of silicon tetrachloride. A modification of this procedure resulted in an improved yield, 70%, of 1,1-dichlorosilacyclohexane, which has also been prepared in an unspecified yield by Hersh⁶, and could be applied with almost

⁴R. R. Widdowson, J. Chem. Soc., 958 (1926).

⁵A. Bygden, Ber., 48, 1236 (1915).

⁶J. M. Hersh, U. S. Patent 2,464,231 (March 15, 1944)
[Original not available for examination; abstracted in C. A.,
43, 8210 (1949)].

equal facility to five- and seven-membered rings^{7,8}. Thus, 1,1-dichlorosilacyclopentane and 1,1-dichlorosilacycloheptane were prepared in yields of 51% and 11%, respectively, by employing essentially the modified procedure⁸. The former compound was obtained in lower yields by other investigators^{9,10}.

Treatment of appropriately substituted trichlorosilanes with difunctional¹¹ Grignard reagents provided a useful route to the syntheses of monofunctional cyclic organosilicon compounds. This technique was used for the preparation of 1-chloro-1-methyl-, 1-chloro-, and 1-chloro-1-phenylsilacyclohexane from 1,5-pentamethylenedimagnesium dibromide and methyltrichlorosilane, trichlorosilane, and phenyltrichlorosilane, respectively, in yields of 62%, 59%, and 64%, respectively. The same procedure was applicable to the syntheses of 1-chloro-1-methyl- and 1-chloro-1-phenylsilacyclopentane in yields of

⁷R. West and E. G. Rochow, Naturwissenschaften, 40, 142 (1953).

⁸R. West, J. Am. Chem. Soc., 76, 6012 (1954).

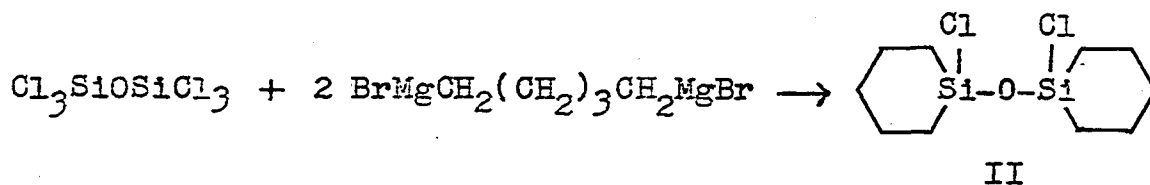
⁹M. Kumada, J. Inst. Polytech. Osaka City Univ., Ser. C., No. 1, 11 (1951) [Original not available for examination; abstracted in C. A., 46, 6082 (1952)].

¹⁰A. F. Plate, N. A. Momma, and Yu. P. Egorov, Doklady Akad. Nauk S. S. S. R., 97, 847 (1954) [Original not available for examination; abstracted in C. A., 49, 10169 (1955)].

¹¹Only the carbon-metal bond(s) will be considered functional in Grignard reagents and organolithium compounds mentioned in this thesis.

47% and 36%, respectively^{5,12}.

1,1'-Oxybis-[1-chlorosilacyclohexane] (II) and 1,1'-bis-[1-chlorosilacyclohexane] were prepared in a similar fashion in yields of 28% and 68%, respectively.



Two generalizations were deduced from some of the aforementioned yields of functional cyclic organosilanes. First, in each series maximum yields were obtained with the six-membered rings, slightly lower yields with the five-membered rings and very low yields with the seven-membered rings. Second, the yield of cyclic product increased as the number of chlorine atoms attached to silicon increased, even though the chance for polymerization increases when the functionality of silicon is increased. The higher yield was attributed to an increased electrostatic field which would facilitate ring closure.

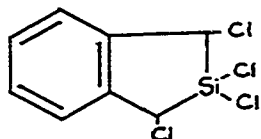
Some five- and six-membered silicon-containing ring compounds having substituents attached to a carbon atom in the

¹²G. D. Lichentwaller, Chemistry Dept., Iowa State College, Ames, Iowa, Information on alicyclic silicon compounds, Private communication (1957).

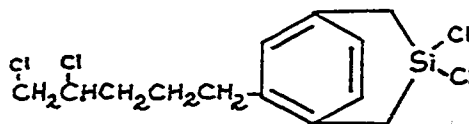
ring have been described¹³. The substantiation of the structures of these compounds is inconclusive since no physical constants were given for them in the abstract of the patent and, furthermore, most of the compounds cited were merely synthesized as intermediates for the preparations of polymers. With these reservation in mind, 1,1,2,3-tetrachlorosilacyclohexane was prepared by allowing the difunctional Grignard reagent of 1,5-dichloropent-1-ene to interact with silicon tetrachloride to give 1,1-dichlorosilacyclohex-2-ene, an intermediate, which was chlorinated between 60-70° to give the desired compound¹³. 1,1,2,3-Tetrachlorosilacycloheptane and 1,1-dichloro-2,3-bis-(3,4-dichlorobutyl)-silacycloheptane were obtained in a similar fashion¹³.

This patent also reported two other novel cyclic silicon compounds in which part of the bicyclic ring system was aromatic. Thus, the reaction of the difunctional Grignard reagents of α, α' -dichloro-o-xylene and 2-(4-pentenyl)- α, α' -dichloro-p-xylene with silicon tetrachloride, followed by the usual chlorination, gave 1,2,2,3-tetrachlorosilaindane (III) and 3,3-dichloro-6-(4,5-dichloropentyl)-3-silabicyclo[3.2.2]-nona-5,7,8-triene (IV)¹³.

¹³J. M. Hersh, U. S. Patent 2,615,033 (October 21, 1952) [Original not available for examination; abstracted in C. A., 47, 9345 (1953)].



III



IV

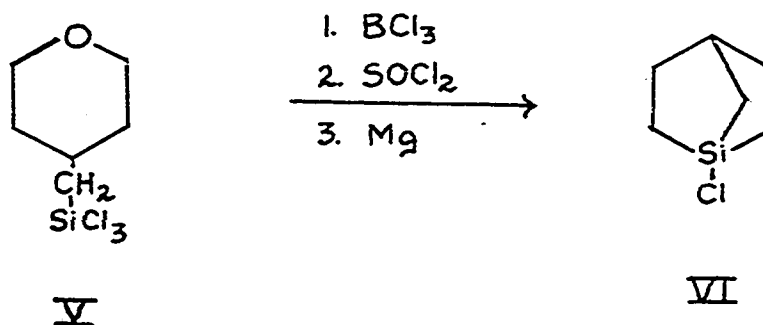
Apropos silacycloalkene types, one such compound was reported and definitely characterized. Petrov *et al.*¹⁴ prepared 1,1-dichlorosilacyclopent-3-ene in a low yield by a direct method, i.e., a high temperature reaction between 3,4-dichlorobut-1-ene and a silicon-copper alloy.

Sommer and Bennett¹⁵ synthesized a novel bicyclic silicon-containing compound for the purpose of elucidating the stereochemical requirements for substitution at a silicon atom. Their multistep synthesis of 1-chloro-1-silabicyclo[2.2.1]-heptane (VI) involved the following steps: the preparation of 4-trichlorosilylmethyltetrahydropyran (V) from the Grignard reagent of 4-bromomethyltetrahydropyran and silicon tetrachloride; cleavage of V with boron trichloride and subsequent treatment of the cleavage product with thionyl chloride; and finally,

¹⁴A. D. Petrov, G. I. Nikishin, N. P. Smetkina, and Yu. P. Egorov, *Izvest. Akad. Nauk S. S. S. R., Otdel. Khim. Nauk*, 947 (1955) [Original available but not translated; translated in *Bull. Acad. Sci. U. S. S. R., Div. Chem. Sci.*, 861 (1955); also abstracted in *C. A.*, 50, 9282 (1956)].

¹⁵L. H. Sommer and O. F. Bennett, *J. Am. Chem. Soc.*, 79, 1008 (1957).

treatment of 1,5-dichloro-3-trichlorosilylmethylpentane with magnesium.



Recently, studies revealed that another type of cyclic organosilicon compound, a ring system containing three or more silicon atoms in the ring, could be obtained by a non-Grignard method. Petrov and Ponomarenko¹⁶ and Nametkin *et al.*¹⁷ converted methylene chloride to 1,1,3,3,5,5-hexachloro-1,3,5-trisilacyclohexane (VII) at 300° in the presence of a silicon-copper alloy. Fritz^{18,19} claimed to have obtained 3,7-dichloro-1,5-bis-(chloromethyl)-3,7-dimethyl-1,3,5,7-tetrasilabicyclo-

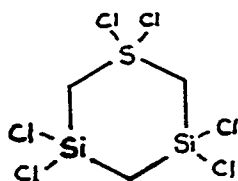
¹⁶A. D. Petrov and V. A. Ponomarenko, Doklady Akad. Nauk S. S. S. R., 93, 387 (1953) [Original not available for examination; abstracted in C. A., 48, 5080 (1954)].

¹⁷N. S. Nametkin, A. V. Topschiev and V. I. Zetkin, ibid., 93, 1045 (1953) [Original not available for examination; abstracted in C. A., 49, 842 (1955)].

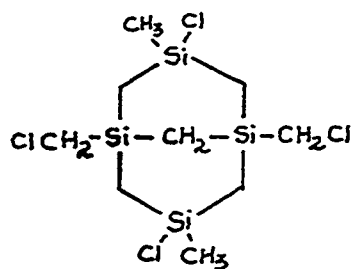
¹⁸G. Fritz, Z. Naturforschung, 12b, 66 (1957).

¹⁹G. Fritz, ibid., 12b, 123 (1957).

[3.3.1]nonane (VIII) from the pyrolysis of trimethylchlorosilane at 800°. Perhaps the assigned structure (VIII) should



VII



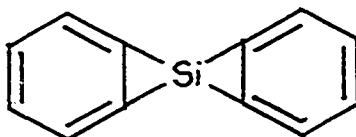
VIII

be held as tentative since its elucidation was based on analytical data, atomic models, and comparison of its physical properties with those of possible open-chained models.

Preparation of Nonfunctional Cyclic Organosilicon Compounds

This section is intended to include synthetic procedures employing only noncyclic functional organosilanes and any other reagents necessary to effect ring closure. Other reactions leading to nonfunctional cyclic types will be mentioned in the section dealing with the properties of cyclic organosilicon compounds.

At the time Hart³ claimed to have prepared 1,1-dichlorosilacyclobutane, he also purported to have prepared a nonfunctional three-membered ring compound (IX) by the sodium



IX

condensation from two moles of o-dichlorobenzene and one mole of silicon tetrachloride. This compound, like the functional one, was supported by meager and questionable evidence and was eventually refuted by Widdowson⁴. An attempt to prepare an alicyclic silicon-containing three-membered ring compound was also unsuccessful²⁰.

To date, a four-membered ring containing silicon has been the smallest ring system synthesized. The two silacyclobutanes were obtained by unique methods. Sommer and Baum²¹ prepared the first such compound by using a procedure involving several steps. Cleavage of 3-bromopropyltrimethylsilane with sulfuric acid, followed by reaction of the resulting symmetrical disiloxane with ammonium chloride and sulfuric acid, yielded 3-bromopropyldimethylchlorosilane which, when treated with magnesium in diethyl ether, afforded 1,1-dimethylsilacyclobutane.

²⁰J. D. Roberts and S. Dev, J. Am. Chem. Soc., 73, 1879 (1951).

²¹L. H. Sommer and G. A. Baum, ibid., 76, 5002 (1954).

West²² independently completed the synthesis of 3,3-dicarbethoxy-1,1-dimethylsilacyclobutane. Using an entirely different approach, he prepared this compound by a ring closure reaction from bis-(iodomethyl)-dimethylsilane, diethyl malonate, and sodium methoxide.

Several nonfunctional cyclic organosilicon compounds were obtained from a difunctional Grignard reagent and a disubstituted dichlorosilane. Compounds prepared in this manner were 1,1-dimethylsilacyclopentane^{9,10}, 1,1-diethylsilacyclopentane⁹, 1,1-dimethylsilacyclohexane²³, and 1,1-diethylsilacyclohexane⁵, the latter being slightly impure; however, the compound was obtained pure by a different method²⁴.

The scope of this reaction can be broadened so as to include a class of cyclic organosilicon compounds heretofore not mentioned. These are aromatic heterocycles containing two hetero atoms, silicon and either oxygen or sulfur. Oita and Gilman²⁵ prepared the first such compounds by dimetalating diphenyl ether and subsequently treating the dimetalated product

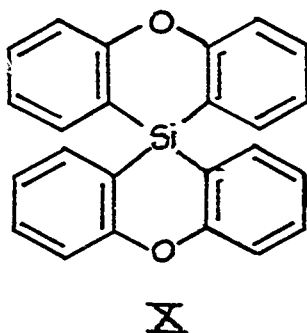
²²R. West, ibid., 77, 2339 (1955).

²³A. F. Plate, N. A. Belikova and Yu. P. Egorov, Izvest. Akad. Nauk S. S. S. R., Otdel. Khim. Nauk, 1085 (1956) [Original available but not translated; abstracted in C. A., 51, 5085 (1957)].

²⁴G. Gruttner and M. Wiernik, Ber., 48, 1473 (1915).

²⁵K. Oita and H. Gilman, J. Am. Chem. Soc., 79, 339 (1957).

with diphenyldichlorosilane, dimethyldichlorosilane, and silicon tetrachloride to give 10,10-diphenyl-, 10,10-dimethylphenoxasilin, and 10,10'-spirobiphenoxasilin (X), respectively.



10,10-Dimethyl- and 10,10-diphenylphenothiasilin-5,5-dioxide were prepared in a similar fashion from the dimetalated product of diphenyl sulfone and the appropriate chlorosilane²⁶.

Goodwin²⁷ reported the preparation of both 1,1,3,3,5,5-hexamethyl-1,3,5-trisilacyclohexane and 1,1,3,3,5,5,7,7-octamethyl-1,3,5,7-tetrasilacyclooctane by the sodium condensation from a mixture of bis-(chloromethyl)-dimethylsilane and bis-(chlorodimethylsilyl)-methane. The former compound was also described in a British patent²⁸.

²⁶K. Oita and H. Gilman, J. Org. Chem., 22, 336 (1957).

²⁷J. T. Goodwin, Jr., U. S. Patent 2,607,791 (August 19, 1952) [Original not available for examination; abstracted in C. A., 48, 13732 (1954)].

²⁸Dow Corning Ltd., British Patent 667,435 (February 27, 1952) [Original not available for examination; abstracted in C. A., 46, 6429 (1952)].

It has been claimed that the thermal decomposition of tetramethylsilane yielded a variety of products among which were included some cyclic organosilicon compounds. The structures were not rigorously established but analytical data, atomic models, and certain chemical and physical properties indicated one fraction to be a mixture of 1,1,3,3,5,5-hexamethyl- and 1,3,3,5,5-pentamethyl-1,3,5-trisilacyclohexane and a second fraction to be 1,3,3,5,7,7-hexamethyl-1,3,5,7-tetrasilabicyclo-[3.3.1]nonane^{29,30}. If the first fraction indeed was a mixture, then the pentamethyl derivative should be readily converted to the hexamethyl derivative by treatment with methyllithium.

Properties of Cyclic Organosilicon Compounds

Chemical properties

Generally speaking, most reactions of functional cyclic organosilicon compounds were analogous to reactions of functional aliphatic and aromatic silanes. Although reactions involving cyclic types were more rapid than similar reactions

²⁹G. Fritz and B. Raabe, Z. Naturforschung, **11b**, 57 (1956).

³⁰G. Fritz and B. Raabe, Z. Anorg. Chem., **286**, 149 (1956).

of open-chained compounds, the mechanism for both types appears to be the same.

Many nonfunctional alicyclic organosilicon compounds were obtained in excellent yields by treating a chloro-substituted silicon-containing ring system with either a Grignard reagent or an organolithium compound. This method of preparing non-functional cyclic organosilicon compounds, although essentially a two step process, was superior to one involving a one step cyclization reaction via a difunctional Grignard reagent. Prepared in this manner were 1,1-dimethyl-, 1,1-diethylsilacyclohexane, 1,1-dimethyl-, 1,1-diethylsilacyclopentane, and 1,1-dimethylsilacyclopent-3-ene^{5,8,9,10,14}.

Whereas Grignard reagents reacted only slowly with a chlorosilacycloalkane, organolithium compounds alkylated the same compound much more readily⁸. 1,1'-Oxybis-[1-chlorosilacyclohexane] and 1,1'-oxybis-[1-chlorosilacyclopentane] interacted smoothly with organolithium compounds¹². Two high boiling compounds, 3,3'-biphenylenebis-[1-phenyl-1-silacyclohexane] and 4,4'-biphenylenebis-[1-phenyl-1-silacyclohexane] were synthesized from 1-chloro-1-phenylsilacyclohexane and 3,3'-biphenylenedilithium and 4,4'-biphenylenedilithium, respectively¹².

Perhaps the most interesting and useful application of an organolithium compound for the synthesis of cyclic silicon compounds was in the preparation of some novel spiranes with

silicon as the spiro atom. These spiranes were generally prepared by allowing a dichlorosilacycloalkane to react with an organodilithium compound, e.g., treatment of 1,5-pentamethylenedilithium with 1,1-dichlorosilacyclopentane and 1,1-dichlorosilacyclohexane gave 5-silaspiro[4.4]nonane and 5-silaspiro[4.5]decane, respectively⁸. 6-Silaspiro[5.5]-undecane could either be prepared as just mentioned or from 1,5-pentamethylenedilithium and silicon tetrachloride, the former being the method of choice⁸.

Hydrolysis of chloro-substituted cyclic organosilicon compounds gave either silanols, disiloxanes or polysiloxanes, depending on the temperature and on whether the compound was mono- or difunctional. Bygden⁵ reported that hydrolysis of 1,1-dichlorosilacyclohexane gave a polymer; however, West⁸, using carefully controlled hydrolysis conditions, obtained 1,1-silacyclohexanediol which was converted to a polymer on warming. 1-Phenyl-1-silacyclohexanol was successfully distilled in vacuo but at elevated temperatures it formed a disiloxane¹². 1-Methyl-1-silacyclohexanol was also easily transformed to the disiloxane. Treatment of 1-chloro-1-silabicyclo[2.2.1]heptane with wet ether yielded the disiloxane¹⁵. Hersh^{6,13} reported the hydrolysis of a number of dichloro-substituted silicon-containing heterocyclic compounds. By employing suitable condensing agents, e.g., sulfuric acid,

he was successful in controlling reaction conditions so as to obtain optimum polymeric structures.

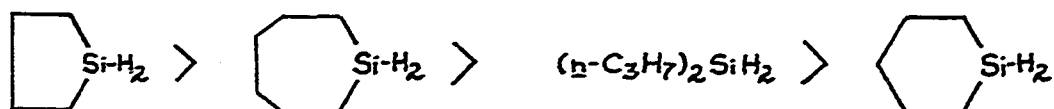
Closely related to the hydrolysis reactions is the formation of alkoxyated derivatives from chlorosilacycloalkanes and an alcohol or alkoxide. 1,1-Dimethoxysilacyclopentane was conveniently obtained from 1,1-dichlorosilacyclopentane and sodium methoxide⁸ or from 1,1-dichlorosilacyclopentane, methanol and pyridine⁹. Higher yields were obtained with the sodium methoxide method.

The chloro-substituted silacycloalkanes were subjected to reduction with either lithium aluminum hydride or lithium hydride. Silacyclopentane, silacyclohexane, and silacycloheptane were prepared by treating the respective dichlorosilacycloalkanes with lithium aluminum hydride⁸. Sommer and Bennett¹⁵ reduced 1-chloro-1-silabicyclo[2.2.1]heptane to 1-silabicyclo[2.2.1]heptane in like fashion. 1-Methylsilacyclohexane⁸ could also be synthesized by a similar procedure but the method of choice was one involving methyldichlorosilane and 1,5-pentamethylenedimagnesium dibromide. 5-Methylsilacyclopentane and 5-methylsilacycloheptane were prepared by the ring closure method⁸. The latter compound was not obtained pure⁸.

Lithium hydride has not been as widely utilized for reduction as has lithium aluminum hydride. In fact the only two compounds reduced with lithium hydride were 1,1-dichloro-

silacyclopentane¹⁰ and 1,1,3,3,5,5-hexachloro-1,3,5-trisilacyclohexane¹⁶.

Two investigations were carried out with the aim of comparing the reactivities of silicon-containing alicyclic systems with their carbon analogs. In one of the studies West³¹ correlated reaction rates with ring size in order to ascertain the importance of "I-strain"³² in such systems. The reaction studied was a base catalyzed hydrolysis in which the hydrogen attached to silicon was replaced by hydroxyl. Thus, the rate studies of silacyclopentane, silacyclohexane, silacycloheptane, and di-*n*-propylsilane showed that the reactivity of the compounds decreased in the order



Since the first hydrogen atom was removed so rapidly, the approximate rates were for the removal of the second hydrogen atom. The free energies of activation and entropies of activation for the various cyclic systems were calculated from the rate data. The order of reactivity was the same as that in

³¹R. West, *J. Am. Chem. Soc.*, **76**, 6015 (1954).

³²H. C. Brown and M. Gerstein, *ibid.*, **72**, 2926 (1950).

the carbocyclic systems and the results were explained in terms of "I-strain".

Sommer and Bennett¹⁵ have studied a bicyclic system containing silicon as one of the bridgehead atoms in an effort of clarify the stereochemical requirements for substitution at a silicon atom. Thus, since 1-chloro-1-silabicyclo[2.2.1]heptane reacted with hydroxide ions and hydride ions under very mild conditions, in sharp contrast to similar reactions with the carbon analog, the authors made the following postulates regarding substitution reactions at a silicon atom: first, a five-membered complex is formed during the reaction; second, the geometry of the complex approximates a trigonal bipyramid; third, the entering group and the group which is displaced need not occupy the apices of the bipyramid. Only the third postulate is completely new.

Ring openings of four-, five, and six-membered ring systems have been carried out with both acidic and basic reagents. In contrast to tetraalkylsilanes, silacyclobutanes underwent violent reactions with sulfuric acid. At 0°, 1,1-dimethylsilacyclobutane gave sym-di-n-propyltetramethyldisiloxane on treatment with sulfuric acid²¹.

The five- and six-membered systems, including a spirane, were also susceptible to ring openings with sulfuric acid. 1,1-Dimethylsilacyclohexane afforded a mixture of disiloxanes and some methane. 5-Silaspiro[4.4]nonane yielded 1,1'-oxybis-[1-

butylsilacyclopentane]. Treatment of 1,1'-oxybis-[1-ethylsilacyclopentane] with sulfuric acid resulted in the formation of sym-tetraethyltetraethylcyclotetrasiloxane.²³

3,3-Dicarbethoxy-1,1-dimethylsilacyclobutane, as well as 1,1-dimethylsilacyclobutane, were cleaved with alcoholic potassium hydroxide^{18,21}. On the other hand, 1,1,3,3,5,5-hexamethyl-1,3,5-trisilacyclohexane was stable to cleavage by strong acids and strong alkalis²⁸. Sommer and Baum²¹ attributed the reactivity of silacyclobutane compounds to angular strain in the ring. West¹⁸ suggested that the total angular strain was no greater in silacyclobutane than in cyclobutanes and, since the former cleaved more rapidly than the latter, his view was that a silacyclobutane ring opening was facilitated because it had available to it mechanisms not available to cyclobutane.

Although 1,1-dimethylsilacyclopent-3-ene was hydrogenated to give the corresponding saturated compound, the reverse reaction, dehydrogenation, did not appear to occur¹⁴. Attempts were made to catalytically dehydrogenate silacyclohexane and 1-methylsilacyclohexane over platinum and palladium at temperatures up to about 500°; only starting materials were recovered. A chromia-alumina catalyst resulted in the oxidation of both compounds to siloxanes⁸.

The cleavage of 10,10'-spirobiphenoxasilin with lithium in dioxane to give bis-(o-hydroxyphenyl)-diphenylsilane was

a valuable aid in elucidating the structure of the cyclic compound²⁵.

Physical properties

Table 1 and Table 2 include all of the cyclic organo-silicon compounds, together with their physical constants, mentioned in the Historical part. None of the compounds described in this dissertation are tabulated in these Tables.

The physical properties of silacycloalkanes are not grossly different from their open-chained counterparts, but some of them do exhibit noteworthy differences. The most unique class of compounds in this respect are the silicon-containing spiranes. They are colorless oils possessing faint camphoraceous odors and, compared with typical organosilicon compounds, they have unusually high densities, refractive indices, melting points, and boiling points. These abnormal properties reach a maximum with 6-silaspiro[5.5]undecane, the boiling point of which was about 45° higher than would be predicted on the basis of the boiling points of linear tetra-alkylsilanes of comparable molecular weight. The abnormal characteristics have been ascribed to the fact that the silicon spiranes are considerably more associated in the condensed phases than are most alkylsilanes⁸.

Table 1. Alicyclic organosilicon compounds^a

Compound	B.p., °C/mm. ^b	n ²⁰ d ²⁰	Ref.
1,1-Dichlorosilacyclohexane	169-170/764 170 ^d	n 1.4697 ^c d 1.1560	(5,6, 7,8)
1-Chloro-1-methylsilacyclohexane	167 ^d	n 1.466 ^c d 1.01	(8)
1-Chlorosilacyclohexane	143 ^d	n 1.467 ^c d 1.018	(8)
1-Chloro-1-phenylsilacyclohexane	77-90/0.09 ^e		(12)
1,1'-Oxybis-[1-chlorosilacyclohexane]	63/0.02 ^e		(12)
1,1'-Bis-[1-chlorosilacyclohexane]	70-73 ^{e,f}		(12)
1-Methylsilacyclohexane	118 ^d	n 1.4462 ^c d 0.809	(8)
1-Silacyclohexane	102 ^d	n 1.4533 ^c d 0.818	(8)
1,1-Dimethoxysilacyclohexane	171 ^d	n 1.4309 ^c d 0.958	(8)

^aCompounds in this dissertation are not included.

^bIn this table the highest value for a constant is recorded when more than one is given unless later investigators indicate the highest value to be in error.

^cn²⁵ and d²⁵.

^dPressure was not given, but it was presumably atmospheric.

^eCompound was not obtained pure.

^fMelting point.

Table 1. (Continued)

Compound	B.p., °C/mm. ^b	n _D ²⁰ d ₄ ²⁰	Ref.
1,1-Silacyclohexanediol	130-132 ^f		(8)
1-Phenyl-1-silacyclohexanol	91/0.02	n 1.5468 d 1.056	(12)
1,1-Dimethylsilacyclohexane	132/740 133 ^d	n 1.4394 d 0.8039	(5,8)
1,1'-Oxybis-[1-methylsilacyclohexane]	253 ^d	n 1.4640 ^c d 0.927	(8)
1,1'-Oxybis-[1-phenylsilacyclohexane]	131-135/0.02	n 1.5546 d 1.050	(12)
1,1'-Bis-[1-phenylsilacyclohexane]	156-164/0.02	n 1.5870 d 1.030	(12)
1,1'-Bis-[1-n-dodecylsilacyclohexane]	200-209/0.02	n 1.4902 d 0.878	(12)
3,3'-Biphenylenebis-[1-phenylsilacyclohexane]	249-252/0.005		(12)
4,4'-Biphenylenebis-[1-phenylsilacyclohexane]	165-165.5 ^f		
1,1-Dichlorosilacyclopentane	143/752	n 1.4651 d 1.151	(8,9,10)
1-Chloro-1-methylsilacyclopentane	132 ^d	n 1.453 ^c d 0.981	(8)
1-Chloro-1-phenylsilacyclopentane	140-145/20 ^e		(12)
1,1-Dimethoxysilacyclopentane	145-151 ^d	n 1.4269 d 0.9623	(8,9)

Table 1. (Continued)

Compound	B.p., °C/mm. ^b	n ₂₀ d ₂₀	Ref.
1,1-Diethoxysilacyclopentane	73.5/38	n 1.4300 d 0.9468	(9)
1-Methylsilacyclopentane	91.5 ^d	n 1.4390 ^c d 0.798	(8)
Silacyclopentane	71/73 ⁴	n 1.4458 d 0.8065	(8,10)
1,1-Dimethylsilacyclopentane	105/74 ² 107 ^d	n 1.43487 d 0.7938	(8,9, 10,14)
1,1-Diethylsilacyclopentane	81/63 159-161 ^d	n 1.4471 d 0.8256	(9,10)
1,1'-Oxybis-[1-ethylsilacyclopentane]	141/34	n 1.4641 d 0.9280	(10,23)
1,1'-Oxybis-[1-n-butylsilacyclopentane]	294/75	n 1.4670 d 0.9125	(23)
1,1'-Oxybis-[1-phenylsilacyclohexane]	127-129/0.02	n 1.5574 d 1.060	(12)
1,1'-Bis-[1-phenylsilacyclopentane]	119/0.005	n 1.5892 d 1.036	(12)
1,1-Dichloro-1-silacyclopent-3-ene	135 ^c	n 1.4782 d 1.2190	(14)
1,1-Dimethylsilacyclopent-3-ene	100.5-101/74 ¹	n 1.4433 d 0.8067	(14)
1,1-Dichlorosilacycloheptane	201 ^d	n 1.452 ^c d 1.065	(8)
1-Methylsilacycloheptane	144 ^{d,e}	n 1.423 ^c	(8)
Silacycloheptane	135 ^{d,e}	n 1.459 ^c d 0.80	(8)

Table 1. (Continued)

Compound	B.p., °C/mm. ^b	n_{D}^{20} d_4^{20}	Ref.
1,1-Dimethylsilacycloheptane	161 ^d	n 1.4335 d 0.780	(8)
1,1-Dimethylsilacyclobutane	81/730	n 1.4270 d 0.7746	(21)
3,3-Dicarbethoxy-1,1-dimethylsilacyclobutane	141-143/15	n 1.4318 ^c d 0.997	(22)
1-Chloro-1-silabicyclo[2.2.1]heptane	54/5	n 1.4956	(15)
Silabicyclo[2.2.1]heptane	131/732 63 ^f		(15)
1,1'-Oxybis[1-silabicyclo[2.2.1]heptane]	76 ^f		(15)
5-Silaspiro[4.4]nonane	178.5 ^d	n 1.4860 ^c d 0.899	(8, 23)
5-Silaspiro[4.5]decane	203 ^d	n 1.4860 ^c d 0.899	(7, 8)
6-Silaspiro[5.5]undecane	203 ^d	n 1.4860 d 0.899	(7, 8)
1,1,3,3,5,5-Hexachloro-1,3,5-trisilacyclohexane	130-140/10 85 ^f		(16, 17)
1,1,3,3,5,5-Hexamethyl-1,3,5-trisilacyclohexane	96/26 200/745	n 1.4606 ^c d 0.846	(17, 27, 28)
1,1,3,3,5,5-Hexaethyl-1,3,5-trisilacyclohexane	136/1		(17)
1,1,3,3,5,5-Hexapropyl-1,3,5-trisilacyclohexane	165/1		(17)

Table 1. (Continued)

Compound	B.p., °C/mm. ^b	n_{D}^{20} d_4^{20}	Ref.
1,1,3,3,5,5-Hexa- butyl-1,3,5- trisilacyclo- hexane	203/3		(17)
1,1,3,3,5,5,7,7- Octamethyl-1,3,5,7- tetrasilacyclo- octane	75/1	$n_D 1.4690^c$	(27)
3,7-Dichloro-1,5- bis-(chloromethyl)- 3,7-dimethyl-1,3,5,7- tetrasilabicyclo- [3.3.1] nonane	106-107 ^f		(19)
1,3,3,5,7,7- Hexamethyl- 1,3,5,7-tetra- silabicyclo [3.3.1] nonane	200 ^g		(30)

^gSublimation temperature.

Detailed Raman spectra¹⁰ were reported for several of the silacyclopentane derivatives as well as for 1,1-dimethylsilacyclopent-3-ene; the most characteristic maximum for the silacyclopentane types appeared at 852 cm⁻¹. Infrared spectra

Table 2. Aromatic cyclic organosilicon compounds^a

Compound	m.p. °C	Ref.
10,10-Diphenylphenoxasilin	178-179	(25)
10,10-Dimethylphenoxasilin	78.5-79	(25)
10,10'-Spirobiphenoxasilin	284-285	(25)
10,10-Diphenylphenothiasilin-5,5-dioxide	208.5-209	(26)
10,10-Dimethylphenothiasilin-5,5-dioxide	160.5-161.5	(26)

^aCompounds in this dissertation are not included.

data regarding silacycloalkanes is quite meager; however, it was an important aid in establishing the structures of certain aromatic heterocycles containing silicon as the hetero atom^{25,26}. Some infrared data is available for dialkylsilacycloalkanes³³.

Although the number of aromatic heterocycles containing silicon is small, excellent thermal stabilities were exhibited by some, especially those containing the phenoxasilin nucleus.

³³G. D. Oshesky and F. F. Bentley, J. Am. Chem. Soc., 79, 2057 (1957).

10,10-Diphenylphenoxasilin and 10,10'-spirobiphenoxasilin appeared to volatilize at about 450° without decomposition. Compounds possessing the phenothiasilin nucleus were not as promising^{25,26}.

Very little has been recorded in the literature concerning applications of cyclic organosilicon compounds. The polymeric siloxanes obtained by condensations of difunctional cyclic types were reportedly useful in lubricants as viscosity and stabilizing agents^{6,13}. Some of the tri- and tetrasilacycloalkanes were cited to be useful as lubricants and hydraulic fluids^{27,28}.

EXPERIMENTAL

All reactions involving organolithium compounds and Grignard reagents were carried out in an atmosphere of dry, oxygen-free nitrogen. Also, all glassware used in these reactions was dried in an oven at 140° and was assembled while hot and while flushing the system with nitrogen. Unless otherwise stated most of the reactions were run in three-necked flasks which could be fitted with equipment such as a Tru-bore stirrer, a condenser or a combination thermometer-nitrogen inlet, and an addition funnel.

The air-oven used in several experiments was a specially designed, electrically heated, insulated, cylindrical oven. The heating element was built in the bottom of the oven. The outer diameter was twelve inches while the inner diameter was five inches, the space between being filled with insulation. The top and bottom were constructed of "Alundum" with the top being removable. Special Claisen type flasks with receivers were designed to fit the oven.

All solvents used with organometallic reagents were commercially available "reagent grade" types, which were stored over sodium wire. The tetrahydrofuran was dried and purified by successively shaking with sodium hydroxide pellets, refluxing over sodium metal for at least 24 hours, and finally distilling immediately before use from lithium aluminum hydride.

Most of the common organic halides were obtained from either Eastman Organic Chemicals or Columbia Organic Chemicals Company. The *m*-bromofluorobenzene and 2,2'-dibromobiphenyl were purchased from Custom Chemical Laboratories and Reaction Products Inc., respectively. The common organosilicon halides were purchased from Dow Corning Corporation. (Chloromethyl)-methyldichlorosilane was procured from Peninsular ChemResearch. Hexachlorodisilane and methyldiphenylchlorosilane were kindly donated by General Electric, while *m*-, *p*-phenylenebis-[trichlorosilane], and 1,2-ethylenebis-[trichlorosilane] were donated by Linde Air Products.

The lithium wire, coated with grease, was carefully wiped and weighed before use. In reactions requiring an excess of lithium, the excess was easily removed by filtering the organolithium solution through a glass-wool plug.

The infrared spectra cited in this dissertation were obtained on a Baird, model B, recording infrared spectrophotometer, property of the Institute for Atomic Research.

All melting points were taken on an electrically heated copper block and are uncorrected.

In general, the silicon analyses were carried out in accordance with the procedure of Gilman *et al.*³⁴ For the fluorophenyl derivatives, nitric acid had to be completely

³⁴H. Gilman, B. Hofferth, H. W. Melvin, Jr. and G. E. Dunn, *J. Am. Chem. Soc.*, **72**, 5767 (1950).

avoided or low results were obtained. The use of sulfuric acid alone or in conjunction with acetic acid, if it was necessary to "wet" the sample, resulted in satisfactory results. The molar refractions were calculated using the bond refraction values of Vogel et al.^{35,36}

Tetraarylsilanes Containing a Halophenyl Group(s)

A detailed description of only one compound of a series is recorded because the reaction conditions and work-up procedures for the other members were generally the same. In those instances in which there is a change in the general procedure, the modification is described in detail.

The infrared spectra of all of the m-fluoro- and m-chloro-phenyl derivatives in either carbon disulfide solutions or as Nujol mulls showed maxima at 9-9.2 μ and 12.7-12.8 μ which were characteristic of an aryl-silicon bond and meta-disubstitution, respectively. The absence of maxima at 2.7 μ and 9.5 μ indicated the compounds to be devoid of Si-OH and Si-O-Si bonds, respectively.

³⁵A. I. Vogel, W. T. Cresswell and J. Leicester, J. Phys. Chem., **58**, 174 (1954).

³⁶A. I. Vogel, W. T. Cresswell, G. H. Jeffery and J. Leicester, J. Chem. Soc., 514 (1952).

Reaction of *m*-fluorophenyllithium with carbon dioxide

Run I. To a rapidly stirred solution containing 0.05 mole of *n*-butyllithium³⁷ in 170 ml. of ether was slowly added a solution of 8.75 g. (0.05 mole) of *m*-bromofluorobenzene in 95 ml. of ether, while not permitting the reaction temperature to rise above -45° . When the addition was complete, the reaction mixture was stirred at -40° for 20 minutes subsequent to pouring it onto a slurry of Dry Ice and ether. The carbonated mixture was allowed to stand at room temperature until the carbon dioxide sublimed, after which hydrolysis was effected with 120 ml. of 5% hydrochloric acid. The organic layer was separated and extracted with three 75-ml. portions of 5% sodium hydrogen carbonate. The combined extracts were boiled to expel dissolved ether and then acidified with concentrated hydrochloric acid. The precipitate was filtered off and crystallized from water to give 4.5 g. (65%) of *m*-fluorobenzoic acid, m.p. $123-124^{\circ}$; reported³⁸ m.p. 124° .

Run 2. The same quantity *n*-butyllithium was used but only 8.0 g. (0.046 mole) of *m*-bromofluorobenzene was employed. The mixture was allowed to warm to room temperature after

³⁷H. Gilman, J. A. Beel, C. G. Brannen, M. W. Bullock, G. E. Dunn and L. S. Miller, J. Am. Chem. Soc., **71**, 1499 (1949).

³⁸A. F. Holleman, Rec. trav. chim., **25**, 330 (1906).

stirring at -40° for ca. 20 minutes. Upon attaining room temperature, the reaction mixture continued to evolve heat and eventually began to reflux. When refluxing subsided (25 minutes), Color Test II³⁹ was negative while Color Test I⁴⁰ was positive. Following carbonation and work-up of the aqueous layer, the crude product was crystallized from water to yield 2.36 g. (37%) of acid, m.p. $122-123^{\circ}$.

Reaction of *m*-fluorophenylmagnesium bromide with carbon dioxide

To a stirred mixture of 1.07 g. (0.044 g. atom) of magnesium turnings, 10 ml. of diethyl ether, and a crystal of iodine was added a solution of 6 g. (0.034 mole) of *m*-bromofluorobenzene in 50 ml. of ether at such a rate as to maintain moderate reflux. When refluxing ceased, the mixture was stirred at room temperature for 15 minutes before carbonating in the same manner as described in the preceding experiment. The yield of *m*-fluorobenzoic acid, m.p. $122-123^{\circ}$, was 2.52 g. (53%).

³⁹H. Gilman and J. Swiss, J. Am. Chem. Soc., 62, 1848 (1940).

⁴⁰H. Gilman and F. Schulze, J. Am. Chem. Soc., 47, 2002 (1925).

Tetrakis-(m-fluorophenyl)-silane

The m-fluorophenyllithium was prepared by allowing 23.6 g. (0.135 mole) of m-bromofluorobenzene in 100 ml. of ether to interact with an ethereal solution containing 0.140 mole of n-butyllithium³⁷. To this stirred mixture was slowly added 5.11 g. (0.030 mole) of silicon tetrachloride dissolved in 20 ml. of ether, while keeping the temperature of the reaction mixture below -35° during the addition. When the addition was complete, the mixture was allowed to warm to room temperature and it was stirred overnight. Subsequent to refluxing for 10 hours, hydrolysis was effected with 100 ml. of 5% hydrochloric acid. A substance, 5.1 g., which was insoluble in both water and ether, was filtered off. This, combined with the 4.9 g. of material isolated from the ethereal layer, was crystallized from petroleum ether (b.p. $77-115^{\circ}$) to give 7.2 g. of white crystals, m.p. $196-197^{\circ}$. Concentration and cooling of the mother liquor yielded an additional 0.7 g. of product; total yield, 7.9 g. (62% based on silicon tetrachloride). The analytical sample, purified by sublimation, melted at $196-197^{\circ}$.

Anal. Calcd. for $C_{24}H_{16}F_4Si$: Si, 6.87. Found: Si, 6.67, 6.64.

Tetrakis-(m-fluorophenyl)-germane

Eight grams (0.037 mole) of germanium tetrachloride in 50 ml. of ether was treated with 248 ml. of an ethereal solution containing 0.178 mole of m-fluorophenyllithium. The mixture was hydrolyzed as described previously. Work-up of the organic layer yielded 7.4 g. of crude product which was dissolved in petroleum ether (b.p. 60-70°), decolorized with Norit-A, filtered, and cooled to deposit 3.6 g. of product, m.p. 194-195°. Another 0.5 g. of material was obtained from the mother liquor; total yield, 4.1 g. (25%). A recrystallization from petroleum ether (b.p. 60-70°) did not raise the melting point.

Anal. Calcd. for $C_{24}H_{16}F_4Ge$: Ge, 16.03. Found: Ge, 16.11, 15.91.

Tris-(m-fluorophenyl)-phenylsilane

To m-fluorophenyllithium, prepared from 23.3 g. (0.133 mole) of m-bromofluorobenzene and 0.133 mole of n-butyllithium³⁷, was added 7 g. (0.033 mole) of phenyltrichlorosilane. Hydrolysis and work-up of the organic layer as described for tetrakis-(m-fluorophenyl)-silane left a gummy residue which was extracted with 80 ml. of benzene and then chromatographed on a 20 cm. x 4 cm. column of alumina. The first eight

fractions yielded 11.7 g. of brown crystalline material which was dissolved in dioxane, decolorized with Norit-A, and filtered. On cooling, 4.5 g. of pale yellow needles, m.p. 190-193°, were deposited. Concentration and cooling of the mother liquor afforded another 2.2 g. of product; total yield, 6.7 g. (51%). The analytical sample, purified by sublimation, melted at 191.5-193°.

Anal. Calcd. for $C_{24}H_{17}F_3Si$: Si, 7.14. Found: Si, 7.04, 7.22.

Bis-(*m*-fluorophenyl)-diphenylsilane

Two hundred milliliters of an ethereal solution containing 0.12 mole of *m*-fluorophenyllithium was slowly added to a stirred solution of 12.7 g. (0.05 mole) of diphenyldichlorosilane in 80 ml. of ether. The mixture was stirred at room temperature for 8 hours and then refluxed for 2 hours. The crude product obtained after working up the reaction mixture as described previously was dissolved in petroleum ether (b.p. 60-70°), decolorized with Norit-A, filtered, and cooled to deposit 4.0 g. of white solid, m.p. 195-196°. From the mother liquor was obtained an additional 0.8 g. of bis-(*m*-fluorophenyl)-diphenylsilane; total yield, 4.8 g. (26%).

Anal. Calcd. for $C_{24}H_{18}F_2Si$: C, 77.39; H, 4.87; Si, 7.53. Found: C, 77.44, 77.54; H, 4.79, 4.77; Si, 7.67, 7.53.

m-Fluorophenyltriphenylsilane

A solution of 25 g. (0.085 mole) of triphenylchlorosilane in 200 ml. of ether was added, during 5 minutes, to 160 ml. of an ethereal solution containing 0.10 mole of m-fluorophenyl-lithium. Following hydrolysis, an insoluble material, 18.74 g., was filtered off and crystallized from glacial acetic acid to give 13.9 g. of m-fluorophenyltriphenylsilane, m.p. 207-208°. Concentration and cooling of the filtrate yielded another 1.3 g. of product; total yield, 15.2 g. (51%).

Anal. Calcd. for $C_{24}H_{19}FSi$: Si, 7.92. Found: Si, 7.68, 7.75.

The original filtrate was dried over sodium sulfate, filtered and the solvent distilled on a steam-bath to leave a brown solid which was soluble in ethanol, benzene, acetic acid, and petroleum ether (b.p. 60-70°); however, attempts to crystallize the material were unsuccessful.

n-Dodecyltris-(m-fluorophenyl)-silane

Sixty milliliters of ether containing 10.9 g. (0.036 mole) of n-dodecyltrichlorosilane was added dropwise to 95 ml. of an ethereal solution containing 0.133 mole of m-fluorophenyl-lithium, while maintaining the temperature below -40°. Work-up in the usual manner left an oil which was distilled under

reduced pressure. The first cut, b.p. 210-216° (0.05 mm.), when redistilled, gave 10.6 g. (62%) of n-dodecyltris-(m-fluorophenyl)-silane, b.p. 197-198° (0.02 mm.), n_D^{20} 1.5358.

Anal. Calcd. for $C_{30}H_{37}F_3Si$: Si, 5.81. Found: Si, 5.68, 5.81.

The compound congealed when cooled in a Dry Ice-acetone bath. It was observed that the compound crystallized on long standing and melted at 35-37°.

Tris-(m-fluorophenyl)-n-hexadecylsilane

An ethereal solution containing 0.133 mole of m-fluorophenyllithium was allowed to interact with 14.7 g. (0.04 mole) of n-hexadecyltrichlorosilane dissolved in 90 ml. of ether. After the usual work-up, the crude product was distilled in vacuo. A small amount of forerun was collected followed by the main fraction, 17.9 g., b.p. 214-217° (0.05 mm.). Redistillation of this fraction yielded 15.6 g. (71%) of a pale yellow liquid which, on cooling to 10°, crystallized to give a yellow solid, m.p. 36-38°.

Anal. Calcd. for $C_{34}H_{45}F_3Si$: C, 75.80; H, 8.42; Si, 5.21. Found: C, 75.96, 76.17; H, 8.42, 8.39; Si, 5.21, 5.29.

Tris-(m-fluorophenyl)-n-octadecylsilane

The compound was prepared from the reaction of 0.10 mole of m-fluorophenyllithium with 11.6 g. (0.03 mole) of n-octadecyltrichlorosilane. Distillation of the crude product gave, as the main fraction, a pale yellow liquid, b.p. 240-260° (0.15 mm.). Redistillation of the main fraction gave 12.1 g. (71%) of tris-(m-fluorophenyl)-n-octadecylsilane, b.p. 234-235° (0.08 mm.). The yellow liquid crystallized, on cooling at 0°, to give a solid, m.p. 38-40°. No suitable solvent or combination of solvents could be found for crystallization of the compound.

Anal. Calcd. for $C_{36}H_{49}F_3Si$: Si, 4.95. Found: Si, 5.07, 4.99.

m-Chlorophenyltriphenylsilane

The m-chlorophenyllithium was prepared in accordance with the method of Gilman and Spatz⁴¹.

A solution of 15 g. (0.078 mole) of m-bromochlorobenzene in 75 ml. of ether was added to 58 ml. of a rapidly stirred ethereal solution containing 0.078 mole of n-butyllithium³⁷, while keeping the reaction temperature below -35° during the

⁴¹H. Gilman and S. M. Spatz, J. Am. Chem. Soc., 66, 621 (1944).

addition. When the addition was complete, the mixture was stirred at -35° for 10 minutes, after which a solution of 14.9 g. (0.05 mole) of triphenylchlorosilane in 170 ml. of ether was added. The mixture was allowed to warm to room temperature and was stirred for 2 hours prior to refluxing overnight. Hydrolysis was effected with 5% hydrochloric acid. Work-up of the organic layer was carried out as described for the m-fluorophenyl derivatives. The crude material, 22 g., was dissolved in ethanol, decolorized with Norit-A, filtered, and cooled to give 12 g. of product, m.p. $156-157^{\circ}$. Concentration of the filtrate gave an additional 2.53 g. of material; total yield, 14.53 g. (78%).

Anal. Calcd. for $C_{24}H_{19}ClSi$: Si, 7.57. Found: Si, 7.63, 7.46.

Bis-(m-chlorophenyl)-diphenylsilane

An ethereal solution containing 8.86 g. (0.035 mole) of diphenyldichlorosilane and 0.13 mole of m-chlorophenyllithium⁴¹ were allowed to react as described in the preceding experiment. Work-up of the organic layer in the usual manner left a brown solid which was dissolved in petroleum ether (b.p. $60-70^{\circ}$) and chromatographed on alumina to give five fractions from which there was obtained 14.4 g. of product melting between $93-111^{\circ}$.

Crystallization of the combined fractions from ethanol gave 11.3 g. (80%) of material, m.p. 110-111°.

Anal. Calcd. for $C_{24}H_{18}Cl_2Si$: Si, 6.92. Found: Si, 6.92, 6.75.

Tris-(m-chlorophenyl)-phenylsilane

An ethereal solution containing 0.11 mole of m-chlorophenyllithium⁴¹ was allowed to interact with 5.5 g. (0.026 mole) of phenyltrichlorosilane. After the usual work-up, the residual oil was dissolved in 250 ml. of petroleum ether (b.p. 60-70°) and chromatographed on alumina to give a white solid which, when crystallized from ethanol, afforded 4.93 g. (43%) of white crystals, m.p. 87.5-89°.

Anal. Calcd. for $C_{24}H_{17}Cl_3Si$: Si, 6.38. Found: Si, 6.44, 6.43.

Tetrakis-(m-chlorophenyl)-silane

Following the reaction of 0.13 mole of m-chlorophenyllithium⁴¹ with 3.82 g. (0.023 mole) of silicon tetrachloride and subsequent work-up of the organic layer, there remained 11.5 g. of crude product which was dissolved in petroleum ether (b.p. 60-70°) and chromatographed on alumina to give 4.9 g. of crystalline material, m.p. 147-149°. Recrystallization from a

mixture of ethanol and benzene gave 4.6 g. (43%) of white crystals, m.p. 148-149°.

Anal. Calcd. for $C_{24}H_{16}Cl_4Si$: Si, 5.92. Found: Si, 5.96, 5.97.

Trialkylsilyl and Triarylsilyl Compounds

1,2-Ethylenebis-[tribenzylsilane]

The benzylmagnesium chloride, prepared from 25.3 g. (0.20 mole) of benzyl chloride and 4.86 g. (0.20 g. atom) of magnesium turnings, was added dropwise to a stirred solution of 5.94 g. (0.02 mole) 1,2-ethylenebis-[trichlorosilane] in 55 ml. of ether. The mixture was refluxed for 12 hours, after which most of the ether was distilled and replaced by xylene. Again, the mixture was refluxed for 50 hours at 100° and then was hydrolyzed with 5% hydrochloric acid. An insoluble material, 10.9 g., was filtered off. The filtrate was dried and the solvents distilled to leave 0.7 g. of crude product. The combined crude material was crystallized thrice from petroleum ether (b.p. 60-70°) and once from ethyl acetate to yield 10.2 g. (81%) of colorless crystals, m.p. 136-137°.

Anal. Calcd. for $C_{44}H_{46}Si_2$: Si, 8.89. Found: Si, 8.95, 8.90.

1,2-Ethylenebis-[tri-2-ethylhexylsilane]

The 2-ethylhexyllithium was prepared essentially in accordance with the method described for n-butyllithium³⁷ from 92 g. (0.0477 mole) of 2-ethylhexyl bromide in 100 ml. of ether and 8.5 g. (1.22 g. atoms) of finely cut lithium wire suspended in 220 ml. of ether. The yield was 68%.

A solution of 7.1 g. (0.024 mole) of 1,2-ethylenebis-[trichlorosilane] in 20 ml. of ether was added slowly to 180 ml. of an ethereal solution containing 0.162 mole of 2-ethylhexyllithium at ice-bath temperature. The mixture was stirred at room temperature overnight, refluxed for 3 hours, and finally hydrolyzed with water. Work-up of the organic layer left a pale yellow oil which was distilled at 0.04 mm. to give a small amount of forerun followed by 9.8 g. (54%) of pale yellow liquid, b.p. 215-220°.

Anal. Calcd. for $C_{50}H_{106}Si_2$: Si, 7.35. Found: Si, 7.52, 7.58.

The infrared spectrum indicated aromatic C-H, Si-OH and Si-O-Si bonds to be absent.

1,2-Ethylenebis-[tri-n-hexadecylsilane]

The n-hexadecyllithium (0.14 mole in 270 ml. of ether) was prepared in 72% yield from 3.08 g. (0.44 g. atom) of lithium

wire and 60 g. (0.197 mole) of n-hexadecyl bromide in accordance with the procedure for n-butyllithium³⁷.

To 150 ml. of an ethereal solution containing 0.047 mole of n-hexadecyllithium, cooled to -10° , was added, during 20 minutes, 2.32 g. (0.008 mole) of 1,2-ethylenebis-[trichlorosilane] in 35 ml. of ether. The mixture was stirred at -7° for 2 hours and at room temperature overnight, after which hydrolysis and work-up of the organic layer was achieved in the usual manner. The crude product, on distillation under reduced pressure, gave 1.05 g. of a waxy solid. The residue was crystallized thrice from ethyl acetate to give a material melting over the range $42-49^{\circ}$. Recrystallization from a mixture of carbon tetrachloride and ethanol at 10° gave 8.4 g. (75%) of product, m.p. $43-45^{\circ}$.

Anal. Calcd. for $C_{98}H_{202}Si_2$: Si, 3.91. Found: Si, 3.83, 3.81.

m-Phenylenebis-[tribenzylsilane]

A solution of 6.92 g. (0.02 mole) of m-phenylenebis-[trichlorosilane] in 55 ml. of ether was added dropwise to a stirred ethereal solution of benzylmagnesium chloride prepared from 25.3 g. (0.20 mole) of benzyl chloride and 4.86 g. (0.20 g. atom) of magnesium turnings. The reaction mixture was refluxed for 12 hours with very little salt forming. Seventy

milliliters of xylene was added and ether was distilled until the temperature rose to 100° . Refluxing was continued at this temperature for 50 hours. The mixture was hydrolyzed with 5% hydrochloric acid and the organic layer was separated and worked up as described for 1,2-ethylenebis-[tribenzylsilane]. The crude viscous oil, which crystallized on standing for 2 days, was refluxed in ethanol and filtered while hot. The insoluble material, 2.67 g., m.p. $140-155^{\circ}$, was crystallized from ethyl acetate to yield 2.20 g. (16%) of prisms, m.p. $155-157^{\circ}$, which were very soluble in dioxane and carbon tetrachloride, moderately soluble in ethyl acetate, and slightly soluble in ethanol.

Anal. Calcd. for $C_{48}H_{46}Si_2$: Si, 8.27. Found: Si, 8.35, 8.26.

The infrared spectrum of the compound in carbon disulfide showed maxima at $12.9\ \mu$ and $14.4\ \mu$ characteristic of meta-disubstitution and a phenyl-silicon bond, respectively. No maxima indicative of Si-OH or Si-O-Si bonds were observed.

From the ethanol filtrate was obtained 7.3 g. of a light brown material which did not distil below 290° (0.10 mm.) and which could not be crystallized from any of the common solvents or solvent mixtures.

m-Phenylenebis-[tri-n-decylsilane]

A solution of 6.6 g. (0.019 mole) of m-phenylenebis-[trichlorosilane] in 35 ml. of ether was added, at -5° , to an

ethereal solution containing 0.148 mole of n-decyllithium, the preparation of which was described under 1,2-ethylenebis-[tri-n-decylsilane]. The mixture was stirred at 0° for 45 minutes, at room temperature for 27 hours, and finally was refluxed for 8 hours. After the usual work-up, the crude product was distilled under reduced pressure. A forerun of 6 g. of decane distilled, followed by 5.3 g. of a slightly higher boiling material. The main fraction yielded 10.8 g. (58%) of m-phenylenebis-[tri-n-decylsilane], b.p. 285-288° (0.03 mm.), n_D^{20} 1.4811, d_4^{20} 0.863.

Anal. Calcd. for $C_{66}H_{130}Si_2$: Si, 5.73; MR, 323.6.
Found: Si, 5.59, 5.76; MR, 323.8.

p-Phenylenebis-[tri-n-decylsilane]

A solution of 5 g. (0.015 mole) of p-phenylenebis-[trichlorosilane] in 30 ml. of ether and 110 ml. of an ethereal solution containing 0.11 mole of n-decyllithium were reacted as described in the preceding experiment. The crude product, which was obtained after a normal work-up of the reaction mixture, was distilled at 0.07 mm. to give 10.2 g. of decane followed by 2.90 g. (20%) of a pale yellow liquid, b.p. 290-294°.

Anal. Calcd. for $C_{66}H_{130}Si_2$: Si, 5.73. Found: Si, 5.94, 5.86.

4-Pentenyltriphenylsilane

The 4-pentenylolithium was prepared by a method similar to that used for *n*-butyllithium³⁷ from 8.0 g. (0.054 mole) of 1-bromo-4-pentene in 70 ml. of ether and 0.9 g. (0.13 g. atom) of lithium wire contained in 60 ml. of ether. The yield of 4-pentenylolithium was 0.03 mole (56%).

A solution of 7.38 g. (0.025 mole) of triphenylchlorosilane in 60 ml. of ether was added to the organolithium compound at -30° . When the addition was complete, the mixture was stirred at 0° for 15 minutes and at room temperature for 11 hours. The mixture was hydrolyzed with water. The organic layer was separated and dried over sodium sulfate. The crude product was distilled at $155-157^{\circ}$ (0.15 mm.) and the distillate was dissolved in ethanol. On cooling to room temperature, 0.65 g. of crystalline material, m.p. $149-152^{\circ}$, was filtered off and the filtrate was cooled by an ice-bath to give a product melting at $44-45^{\circ}$. Recrystallization from ethanol yielded 5.5 g. (67%) of 4-pentenyltriphenylsilane, m.p. $45-46^{\circ}$.

Anal. Calcd. for $C_{23}H_{24}Si$: Si, 8.54. Found: Si, 8.61, 8.55.

1,5-Pentamethylenebis-[triphenylsilane]

Method A. The procedure was similar to one described by Merten and Gilman⁴².

A mixture of 26 g. (0.10 mole) of triphenylsilane, 3.4 g. (0.01 mole) of 4-pentenyltriphenylsilane, 0.32 g. (0.0013 mole) of benzoyl peroxide, and 25 ml. of *n*-hexane was stirred at 80° for 20 hours, after which the excess triphenylsilane was distilled at 148-160° (0.7 mm.), leaving a brown, gummy material which was extremely soluble in the common organic solvents. The crude product was crystallized from a mixture of ethanol and methyl ethyl ketone to yield 4.18 g. of material, m.p. 140-143°. Two recrystallizations from a mixture of ethanol and ethyl acetate afforded 3.8 g. (65%) of 1,5-pentamethylenebis-[triphenylsilane], m.p. 146-147°.

Anal. Calcd. for $C_{41}H_{40}Si_2$: Si, 9.53. Found: Si, 9.70, 9.48.

Method B. The 1,5-pentamethylenedilithium was prepared in accordance with the method of West and Rochow⁴³.

A solution of 20 g. (0.087 mole) of 1,5-dibromopentane in 80 ml. of ether was added to a rapidly stirred suspension of

⁴²H. Merten and H. Gilman, J. Am. Chem. Soc., 76, 5798 (1954).

⁴³R. West and E. G. Rochow, J. Org. Chem., 18, 1739 (1953).

5.25 g. (0.757 g. atom) of lithium ribbon (1/4 inch x 1/32 inch), cut into approximately 1/4 inch squares, in 100 ml. of ether. The reaction was initiated at room temperature with 3 ml. of the bromide solution, while the remainder was added, during 2 hours, at -10° . When the addition was complete, the mixture was stirred at 10° for 30 minutes and then was cooled to -20° . A double titration⁴⁴ indicated the yield to be 40%. To the organodilithium compound, cooled to -20° , was added 17.4 g. (0.059 mole) of triphenylchlorosilane in 160 ml. of ether. When the addition was complete, the mixture was allowed to warm to room temperature and was stirred overnight. The mixture was hydrolyzed and worked up in the usual manner. The crude product was crystallized from a mixture of ethanol and ethyl acetate to give 4.4 g. of white crystals, m.p. $145-146^{\circ}$, which did not depress the melting point of the compound from the preceding experiment when admixed with it. Concentration of the filtrate and subsequent addition of ethanol gave another 4 g. of product; total yield, 8.4 g. (48%).

3,3'-Biphenylenebis-[triphenylsilane]

To 75 ml. of a stirred ethereal solution containing 0.038 mole of *n*-butyllithium³⁷ and cooled to -30° was added, during 10

⁴⁴H. Gilman and A. H. Haubein, J. Am. Chem. Soc., **66**, 1515 (1944).

minutes, a solution of 6 g. (0.019 mole) of 3,3'-dibromobiphenyl in 30 ml. of ether. When the addition was complete, the mixture was stirred at room temperature for 6 hours and then was refluxed for 15 minutes. To this stirred, insoluble organodilithium compound was added a solution of 11.3 g. (0.038 mole) of triphenylchlorosilane in about 100 ml. of ether. The mixture was refluxed for 45 minutes, whence 100 ml. of benzene was added and the mixture distilled until an internal temperature of 53° was reached. After refluxing at this temperature for 15 minutes, the mixture was hydrolyzed with water and an insoluble material was filtered off, dried, and crystallized from a mixture of water and dioxane to give 6.85 g. of product, m.p. $220-223^{\circ}$. Recrystallization from the same solvent mixture raised the melting point to $221-223^{\circ}$. From the filtrate was obtained an additional 2.0 g. of material; total yield, 8.85 g. (69%).

Anal. Calcd. for $C_{48}H_{38}Si_2$: Si, 8.37. Found: Si, 8.06, 8.07.

Organosilylmethylolithium Compounds

(Chloromethyl)-methyldiphenylsilane (impure)

Seven hundred milliliters of an ethereal solution containing 0.765 mole of phenyllithium⁴⁵ was added dropwise to a

⁴⁵R. G. Jones and H. Gilman in R. Adams, "Organic Reactions", John Wiley & Sons, Inc., New York, N. Y., 1951, Vol. 6, p. 354.

rapidly stirred solution of 60 g. (0.368 mole) of (chloromethyl)-methyldichlorosilane in about 125 ml. of ether. The rate of addition was such as to maintain moderate reflux and required 2.3 hours. When the addition was complete, Color Test I was negative. Subsequently, the mixture was hydrolyzed with water. The organic layer was separated, dried over sodium sulfate, and the solvent was distilled off. Distillation of the residue through a short-path Vigreux column gave 76.0 g. (84%) of colorless liquid, b.p. 100-102° (0.012 mm.), n_D^{20} 1.5810, d_4^{20} 1.106.

Anal. Calcd. for $C_{14}H_{15}ClSi$: C, 68.11; H, 6.13; MR, 74.80. Found: C, 68.96; H, 5.88; MR, 74.40.

Though the compound is slightly impure, the impurity did not interfere with subsequent reactions.

(Chloromethyl)-methyldibenzylsilane (impure)

To an ethereal solution containing 0.60 mole of benzyl magnesium chloride was added a solution of 20 g. (0.123 mole) of ether. The addition was carried out at a rate sufficient to maintain moderate reflux and required about 1 hour. After refluxing the mixture for 2 days, the precipitate became so dense that stirring became very inefficient. The reaction mixture was poured into a mixture of ice and 5% hydrochloric

acid. The organic layer was worked up as described in the preceding experiment. Distillation of the crude product gave 4.2 g. of forerun, mainly bibenzyl, followed by the main fraction, 24.81 g. (74%), b.p. 115-120° (0.02 mm.), n_D^{20} 1.5715, d_4^{20} 1.067.

Anal. Calcd. for $C_{16}H_{19}ClSi$: C, 69.94; H, 6.47; MR, 83.9. Found: C, 72.59; H, 6.78, MR, 84.4.

The analysis indicates an impurity to be present. This impurity, however, did not interfere with subsequent reactions. An attempt is going to be made to further purify the material.

(Chloromethyl)-di-n-tetradecylmethylsilane (attempted)

A solution of 39.7 g. (0.243 mole) of (chloromethyl)-methyldichlorosilane and 600 ml. of an ethereal solution containing 0.52 mole of n-tetradecyllithium was stirred at room temperature overnight. Work-up of the organic layer in the usual manner, followed by distillation at 0.005 mm., yielded eight fractions, each boiling over a wide range, and none of which had experimental molar refractions which agreed with the calculated value.

(Chloromethyl)-di-n-dodecylmethylsilane (attempted)

An ethereal solution of 30 g. (0.182 mole) of (chloromethyl)-methyldichlorosilane and 0.43 mole of n-dodecylmagnesium

bromide was refluxed for 1 hour with no sign of reaction. Ether was distilled and the mixture was refluxed at 70° for 2 hours and at 80° overnight. After the usual work-up of the organic layer, the crude material was distilled at 0.05 mm. to give nine fractions, each boiling over a wide range. None of the fractions had molar refractions which agreed with the calculated value.

[(Methyldiphenylsilyl)-methyl]-diphenylmethanol

A mixture of 3 g. (0.433 g. atom) of lithium ribbon, cut into small pieces, 6 g. (0.0243 mole) of (chloromethyl)-methyldiphenylsilane, and 50 ml. of benzene was refluxed for 11.5 hours. The organolithium solution was cooled and filtered into a three-necked flask. To this stirred mixture was added a solution of 4.43 g. (0.024 mole) of benzophenone in 50 ml. of benzene. Color Test I⁴⁰ was negative after adding about one-half of the solution. Subsequently, the reaction mixture was poured into a saturated ammonium chloride solution. The organic layer was worked up in the usual manner. The crude product was distilled at 0.005 mm. in an electrically wired air-oven. After collecting a small amount of forerun, mainly unreacted benzophenone, the main fraction distilled over the range 130-186° to give 4.35 g. (45%) of milky material which solidified upon being agitated. Two recrystallizations from

petroleum ether (b.p. 60-70°) and one crystallization from 95% ethanol gave 2.96 g. (31%) of white needles, m.p. 89-90°.

Anal. Calcd. for $C_{27}H_{26}OSi$: Si, 7.11. Found: Si, 7.00, 6.92.

[(Methyldibenzylsilyl)-methyl]-diphenylmethanol

A mixture of 2.67 g. (0.385 g. atom) of lithium ribbon, 4 g. (0.0145 mole) of (chloromethyl)-methyldibenzylsilane and 55 ml. of *n*-pentane was refluxed for 18 hours. The slightly cloudy organolithium compound was filtered through a glass-wool plug into a three-necked flask and to the resulting stirred solution was added 2.73 g. (0.015 mole) of benzophenone dissolved in 40 ml. of *n*-pentane. A white precipitate formed during the addition which required 10 minutes. After hydrolysis with water, diethyl ether was added to clear up the organic layer which was worked up in the usual manner. Distillation of the solvents from the organic layer left a solid which was crystallized from petroleum ether (b.p. 60-70°) to give 4.03 g. (66%) of product, m.p. 105.5-106.5°.

Anal. Calcd. for $C_{29}H_{30}OSi$: C, 82.42; H, 7.16; Si, 6.64. Found: C, 82.62; H, 7.13; Si, 6.62, 6.72.

Metalation Reactions

Reaction of *n*-butyllithium with furan

Eighteen milliliters of a diethyl ether solution containing 0.025 mole of *n*-butyllithium³⁷ was added, during 6 minutes, to a stirred solution of 23 g. (0.34 mole) of redistilled furan in 20 ml. of tetrahydrofuran (THF). The reaction temperature was kept between -25 and -30° during the addition. Subsequently, the mixture was poured onto a slurry of Dry Ice and diethyl ether. Prior to separation of the two layers and subsequent to hydrolysis, 50 ml. of diethyl ether was added to the mixture. The aqueous layer was boiled until most of the THF had been expelled and then was acidified with concentrated hydrochloric acid. The organic layer was extracted twice with 5% sodium hydroxide. The extracts, together with the aqueous layer, were acidified and extracted with ether. Distillation of the ether left a residue which was sublimed at 70° and 0.007 mm. to give 2.21 g. (80% based on *n*-butyllithium) of pure 2-furoic acid, m.p. 131-132°.

Reaction of phenyllithium with dibenzothiophene

The phenyllithium was prepared by adding 39 g. (0.248 mole) of bromobenzene in 25 ml. of tetrahydrofuran (THF),

during 40 minutes while keeping the temperature below -50° , to a stirred suspension of 5.25 g. (0.757 g. atom) of lithium wire in 70 ml. of THF. After stirring below -50° for 2 hours, the mixture was filtered and stored in a refrigerator. A single acid titration indicated the concentration to be 0.91 molar.

To a stirred solution of 5.0 g. (0.027 mole) of dibenzothiophene in 60 ml. of THF was added rapidly 30 ml. of a 0.91 M phenyllithium solution, while cooling the mixture with an ice-bath. The reaction mixture was stirred at room temperature for 5 hours prior to carbonation. The carbonated mixture was hydrolyzed with water, more ether was added, and the two layers were separated. The aqueous layer was acidified with hydrochloric acid and filtered while hot to give 4.26 g. of crude acid, m.p. $245-248^{\circ}$. One crystallization from acetic acid yielded 3.78 g. (62%) of 4-dibenzothiophenecarboxylic acid, m.p. $262-264^{\circ}$, identified by mixed melting point.

Reaction of lithium with cyclopentadiene

Run 1. A solution of 4.03 g. (0.061 mole) of cyclopentadiene in 30 ml. of tetrahydrofuran (THF) was added to a rapidly stirred suspension of 2 g. (0.288 g. atom) of lithium in 40 ml. of THF. Initially, about 5 ml. of the cyclopentadiene solution was added. After 15 minutes the reaction mixture became pale yellow and in another 5 minutes bubbles began to evolve around

the pieces of lithium. The remaining cyclopentadiene solution was added, during 45 minutes, while cooling the mixture with an ice-bath. The mixture was stirred at room temperature for 30 minutes before filtering it through a glass-wool plug into a stirred solution of 10.9 g. (0.06 mole) of benzophenone in 35 ml. of THF. The orange mixture was stirred at room temperature for 21 hours and then was poured into a mixture of ice and water. The organic layer was separated and most of the solvent was evaporated under a stream of dry air. The red residue was refluxed in petroleum ether (b.p. 28-38°) and filtered to leave a brown, gummy material. The petroleum ether was slowly evaporated under reduced pressure to leave orange crystals which were washed with 95% ethanol, filtered, and dried to give 4.35 g. of orange needles. An additional 0.53 g. of product, m.p. 72-75°, was obtained from the mother liquor. The total yield of diphenylfulvene, m.p. 75-77°, was 4.88 g. (35%). A mixed melting point with an authentic sample was undepressed.

Run 2. In this run, there were used 8.05 g. (0.122 mole) of cyclopentadiene and 3.4 g. (0.49 g. atom) of lithium. The addition required 2.5 hours. Treatment of the organolithium compound with benzophenone yielded 12.78 g. (45%) of diphenylfulvene, m.p. 75-77°.

Reaction of lithium with fluorene

A solution of 5 g. (0.03 mole) of fluorene in 35 ml. of tetrahydrofuran (THF) was added, during 1.5 hours, to a stirred suspension of 1.23 g. (0.178 g. atom) of lithium wire contained in 10 ml. of THF. The color of the mixture, which was periodically cooled with a water-bath during the addition, changed from green to orange. When the addition was complete, the mixture was stirred at room temperature for 50 minutes and then was poured onto a slurry of Dry Ice and diethyl ether. Following hydrolysis with water, the aqueous layer was separated, boiled to expel THF and diethyl ether, filtered, and acidified with hydrochloric acid to give a pale yellow solid which was filtered and dried to give 4.85 g. of crude product, m.p. 223-226°. Crystallization from acetic acid afforded 4.46 g. (71%) of needles, m.p. 230-232°, which showed no depression in melting point when admixed with an authentic sample of 9-fluorene-carboxylic acid.

Reaction of lithium with 9-phenylfluorene

A mixture of 4.0 g. (0.0165 mole) of 9-phenylfluorene, 1.7 g. (0.245 g. atom) of lithium wire, and 45 ml. of tetrahydrofuran was stirred at room temperature for 4 hours, while periodically cooling with a cold-water-bath. The reaction

mixture was poured jetwise onto a slurry of Dry Ice and ether. Following hydrolysis with water, the organic layer was separated and extracted twice with 5% sodium hydroxide. The basic extracts and the aqueous layer were acidified with hydrochloric acid to give a total of 1.81 g. (38%) of acid, m.p. 180-182°, which showed no depression in melting point when admixed with an authentic sample of 9-phenylfluorene-carboxylic acid.

Preparation of 9,9-diphenylfluorene

The procedure was similar to one described by Clarkson and Gomberg⁴⁶.

An ethereal solution containing 0.344 mole of 2-biphenyllithium⁴⁷ was added to a stirred solution of 62.6 g. (0.344 mole) of benzophenone in 170 ml. of diethyl ether. Color Test I⁴⁰ became negative after 90% of the benzophenone solution had been added. The mixture was hydrolyzed with water and the organic layer was worked up in the usual manner. Evaporation of the solvent under a stream of dry air left a solid which was crystallized from ethanol to yield 82 g. of needles, m.p. 86-88°. Another 15 g. of 2-biphenyldiphenylcarbinol, m.p.

⁴⁶R. G. Clarkson and M. Gomberg, J. Am. Chem. Soc., 52, 2881 (1930).

⁴⁷H. Gilman and K. Oita, J. Org. Chem., 20, 862 (1955).

85-87°, was obtained from the mother liquor; total yield, 97 g. (84%).

9,9-Diphenylfluorene, m.p. 226-228°, was obtained by refluxing the 2-biphenylyldiphenylcarbinol in glacial acetic acid.

Reaction of lithium with triphenylmethane (attempted)

A mixture of 5 g. (0.02 mole) of triphenylmethane, 0.8 g. (0.115 g. atom) of lithium wire, and 40 ml. of tetrahydrofuran (THF) was stirred at room temperature for 5 days. The THF was distilled off to leave 4.71 g. (94%) of unchanged triphenylmethane, m.p. 90-92°, identified by mixed melting point.

Cleavage of a Carbon-Carbon Bond by Lithium

Reaction of lithium with 9,9-diphenylfluorene

A mixture of 6.0 g. (0.019 mole) of 9,9-diphenylfluorene, 2.0 g. (0.29 g. atom) of lithium wire, and 50 ml. of tetrahydrofuran was stirred at room temperature for 15 hours. During the course of the reaction the color of the mixture became blue, then green, and finally reddish-brown. The organic layer was separated and dried over sodium sulfate after hydrolyzing with water. Distillation of the solvent left a material

which was crystallized from a minimum of ethanol to give 3.56 g. of colorless needles, m.p. 143-144°, identified by mixed melting point with an authentic sample of 9-phenylfluorene. An additional 0.32 g. of product was obtained from the mother liquor; total yield, 3.88 g. (85%).

When the reaction time was limited to 1.75 hours, only a 25% yield of 9-phenylfluorene was obtained.

Cleavage Reactions of Some Noncyclic Organosilicon Compounds

Preparation of diphenylsilane

The procedure used was a modification of one described by Benkeser et al.⁴⁸

To a suspension of 9.75 g. (0.257 mole) of lithium aluminum hydride in 200 ml. of tetrahydrofuran (THF) was added, during 30 minutes, a solution of 127 g. (0.50 mole) of diphenyldichlorosilane in about 40 ml. of THF. When the addition was complete, the mixture was refluxed for 1 hour, after which ethyl acetate was added until the excess lithium aluminum hydride was destroyed. Subsequently, the mixture was poured into cold 8 N hydrochloric acid. About 100 ml. of diethyl ether was added and the organic layer was separated from the gray aqueous

⁴⁸R. A. Benkeser, H. Landesman, and D. J. Foster, J. Am. Chem. Soc., **74**, 648 (1952).

layer which was washed with two portions of diethyl ether. The combined organic layer was dried over sodium sulfate and the solvents were distilled to leave an oil which was distilled at 17 mm. to give as the main fraction 82 g. (89%) of diphenylsilane, b.p. 133-136°, n_D^{20} 1.5797.

Preparation of methyldiphenylsilane

This compound was prepared according to a modified procedure of Benkeser and Foster.⁴⁹

A solution of 25 g. (0.107 mole) of methyldiphenylchlorosilane in 25 ml. of tetrahydrofuran (THF) was added dropwise, during 30 minutes, to a stirred suspension of 2.66 g. (0.07 mole) of lithium aluminum hydride in 90 ml. of THF. When the addition was complete, the mixture was stirred at room temperature overnight and refluxed for 1 hour. The excess lithium aluminum hydride was destroyed with ethyl acetate. Hydrolysis and work-up of the mixture was achieved in the manner described in the preceding experiment. Distillation of the crude product under reduced pressure gave 16.42 g. (78%) of methyldiphenylsilane, b.p. 137-139° (14 mm.), n_D^{20} 1.5724; reported n_D^{20} 1.5747.

⁴⁹R. A. Benkeser and D. J. Foster, ibid., 74, 5314 (1952).

Reaction of lithium with diphenylsilane

A mixture of 6 g. (0.033 mole) of diphenylsilane, 0.45 g. (0.065 g. atom) of finely cut lithium wire, and 40 ml. of tetrahydrofuran was stirred at room temperature for 84 hours, during which Color Test I⁴⁰ remained negative. After 7 hours the mixture was very milky and the pieces of lithium were coated black. The reaction mixture was filtered, hydrolyzed, and worked up as described above. Distillation of the crude product gave 3.25 g. (77% based on the cleavage of one phenyl group) of liquid, b.p. 117-119° (0.01 mm.), which crystallized when seeded with triphenylsilane. Crystallization of the distillate from methanol gave 2.95 g. (70%) of triphenylsilane, m.p. 43-44°, identified by mixed melting point.

Reaction of lithium with tri-2-biphenylsilane

Two grams (0.0041 mole) of tri-2-biphenylsilane⁴⁷, 1.7 g. (0.245 g. atom) of finely cut lithium wire, and 15 ml. of tetrahydrofuran (THF) were stirred between 0-5° for 30 minutes, after which another 15 ml. of THF was added. The mixture was stirred for an additional 1.5 hours between 0-5° subsequent to pouring it into a mixture of ice and water. The organic layer was separated and worked up in the usual manner. The residue, after distillation of the solvent, was sublimed at 85° and

17 mm. to give 1.07 g. (85% based on the cleavage of two bi-phenylyl groups) of biphenyl, m.p. 68-69^o, identified by mixed melting point.

The infrared spectrum of the residual material in carbon disulfide and in carbon tetrachloride showed a sharp peak at 2.8 μ and a broad band between 9-10 μ indicative of Si-OH and Si-O-Si bonds, respectively. No peak characteristic of Si-H was observed.

Reaction of lithium with methyldiphenylsilane

Run 1. A mixture of 3.5 g. (0.0177 mole) of methyldiphenylsilane, 1.9 g. (0.274 g. atom) of lithium wire, and 40 ml. of tetrahydrofuran (THF) was stirred at room temperature for 1.5 hours, while periodically cooling with a cold water-bath. The mixture was filtered into another flask after which was added, during 20 minutes, a solution of 5.66 g. (0.019 mole) of triphenylchlorosilane. The mixture was hydrolyzed with water and an insoluble product was filtered off to give 3.25 g. (66% based on triphenylchlorosilane) of hexaphenyldisilane, m.p. 356-360^o, which showed no depression in melting point when admixed with an authentic specimen.

The organic layer was separated and worked up in the usual manner. The residual oil partially crystallized on standing. The solid was warmed in ethanol and filtered. The solid was

again washed with petroleum ether (b.p. 28-38°) and filtered to give 0.7 g. of material (crop 1) melting over the range 114-126°. Concentration of the combined filtrates left more solid which was crystallized from ethanol to give 2.14 g. of product (crop 2) melting over the range 124-130°. The infrared spectra of the two crops were similar except for a maximum at 2.8 μ in crop 2.

Crop 1 was dissolved in benzene and chromatographed on alumina to give a white solid which yielded 0.24 g. of material, m.p. 138.5-140°, after crystallization from ethanol. A mixed melting point with 1,2-dimethyl-1,1,2,2-tetraphenyldisilane was 140-142°. A mixed melting point with methylpentaphenyldisilane was 117-126°.

Crop 2 was dissolved in petroleum ether (b.p. 60-70°) and chromatographed on alumina. Elution was effected successively with petroleum ether, benzene, and methanol. From the petroleum ether eluates were obtained two fractions melting over the ranges 136-145° and 110-125°, respectively, after crystallization from ethanol. A waxy material was obtained from the benzene eluate and a small amount of oil from the methanol eluate. Further attempts to purify the above fractions were unsuccessful.

Run 2. The same quantities of reactants and the same reaction conditions were used in this run as in the previous one. The cleavage product was added, during 40 minutes, to

5.63 g. (0.019 mole) of triphenylchlorosilane in 40 ml. of THF. The mixture was stirred at room temperature overnight, then hydrolyzed with water, and filtered to give 2.55 g. (52% based on triphenylchlorosilane) of hexaphenyldisilane, m.p. 362-364°.

The organic layer was worked up as described previously. The residual material was distilled at 0.005 mm. to give the following fractions: (1) 0.24 g., b.p. 54°, n_D^{20} 1.5720; (2) 0.51 g., b.p. 54-55°, n_D^{20} 1.5725; (3) 0.38 g., b.p. up to 85°, n_D^{20} 1.5723; (4) 1.21 g., b.p. 120-130°, n_D^{20} 1.6092. Fractions 1 and 2 were identical with methyldiphenylsilane with respect to refractive index and infrared spectrum. The yield, based on the cleavage of one phenyl group, was 43%. Fraction 3 appeared to be a mixture of fractions 2 and 4. Fraction 4 eventually crystallized and had an infrared spectrum identical with that of triphenylsilane. The yield was 25% based on triphenylchlorosilane. Treatment of some of this fraction with phenyllithium gave tetraphenylsilane.

Reaction of lithium with triphenylsilane

Run 1. A mixture of 8 g. (0.031 mole) of triphenylsilane, 0.25 g. (0.036 g. atom) of lithium wire, and 60 ml. of tetrahydrofuran (THF) was stirred at room temperature for 3.75 hours prior to treatment with 3.0 g. (0.028 mole) of trimethylchlorosilane in 5 ml. of THF. The mixture was hydrolyzed with water

and an insoluble material was filtered off to give 0.96 g. of tetraphenylsilane, m.p. $232-234^{\circ}$, identified by mixed melting point. The organic layer was worked up as usual to leave an oil which deposited 0.95 g. of solid, m.p. $219-223^{\circ}$, after shaking in petroleum ether (b.p. $26-38^{\circ}$). Recrystallization from ethyl acetate gave 0.84 g. of tetraphenylsilane, m.p. $234-235^{\circ}$; total yield, 1.80 g. (30% based on lithium).

The petroleum ether filtrate was evaporated and the residue was crystallized from ethanol to give 1.34 g. of product, m.p. $95-104^{\circ}$. Two recrystallizations from ethanol yielded 1.07 g. of 1,1,1-trimethyl-2,2,2-triphenyldisilane, m.p. $107-108^{\circ}$, whose melting point was not depressed when admixed with an authentic specimen. After distilling the ethanol from the filtrate, the residual oil, on standing for ca. 1 week, deposited a crystalline material which was filtered, washed with methanol, and dried to give a product melting over the range $95-106^{\circ}$. This was washed with petroleum ether (b.p. $28-38^{\circ}$) to give 0.03 g. of tetraphenylsilane. The petroleum ether was evaporated and the residue was crystallized from ethanol to yield 0.3 g. of 1,1,1-trimethyl-2,2,2-triphenyldisilane.

The ethanol was removed and the residual oil was distilled under reduced pressure to give the following fractions: (1) 0.50 g., b.p. $175-180$ (14 mm.), n_D^{20} 1.5763; (2) 0.75 g., b.p. $118-120^{\circ}$ (0.005 mm.), n_D^{20} 1.5902; (3) 1.31 g., b.p. $125-128^{\circ}$ (0.005 mm.); (4) 0.48 g., b.p. $134-140^{\circ}$ (0.005 mm.). Treatment

of fraction 1 with phenyllithium gave 0.06 g. of tetraphenylsilane and 0.13 g. of 1,1,1-trimethyl-2,2,2-triphenyldisilane; fraction 2 gave 0.45 g. of tetraphenylsilane; and fraction 3 gave 1.22 g. of tetraphenylsilane and 0.08 g. of 1,1,1-trimethyl-2,2,2-triphenyldisilane. Fraction 4 was crystallized from ethanol to give 0.15 g. of 1,1,1-trimethyl-2,2,2-triphenyldisilane, m.p. 107-108°. The total yield of the latter was 1.73 g. (58% based on the lithium cleavage of tetraphenylsilane).

Run 2. Sixteen grams (0.062 mole) of triphenylsilane, 0.25 g. (0.036 g. atom) of lithium, and 60 ml. of THF were stirred at room temperature for 7.5 hours, after which 3.0 g. (0.028 mole) of trimethylchlorosilane was added. Work-up as described in run 1 yielded an insoluble material which was combined with material obtained by treating the residue from the organic layer with petroleum ether (b.p. 28-38°) to give a total of 3.09 g. of white powder melting over the range 228-290°. This was warmed in benzene and filtered while hot to give 0.8 g. of insoluble product which, after crystallization from dioxane, yielded 0.5 g. of hexaphenyldisilane, m.p. 363-366°. A mixed melting point with an authentic sample showed no depression. The filtrate was evaporated and the residue was refluxed in ethyl acetate and filtered while hot to give an additional 0.36 g. of hexaphenyldisilane, m.p. 363-366°. The filtrate deposited 1.48 g. of tetraphenylsilane, m.p. 232-234°.

Concentration of the mother liquor afforded an additional 0.15 g. of product.

The ethyl acetate filtrate was evaporated and the residue was distilled at 13 mm. to give the following fractions: (1) 0.96 g., b.p. up to 180° , n_D^{20} 1.5870; (2) 1.91 g., b.p. $180-205^{\circ}$; (3) 4.71 g., b.p. $205-210^{\circ}$; (4) 3.89 g., b.p. 210° ; (5) b.p. above 250° . Fraction 1 yielded a liquid, n_D^{20} 1.5783, after treatment with methyllithium. Fractions 2-4 crystallized on standing and were shown to be triphenylsilane by mixed melting point and infrared spectrum. Fraction 5 was refluxed in petroleum ether (b.p. $28-38^{\circ}$) and filtered. The insoluble material was crystallized from ethyl acetate to give 0.1 g. of tetraphenylsilane. The filtrate was evaporated and the residue was crystallized once from petroleum ether (b.p. $60-70^{\circ}$), twice from absolute ethanol, and once from petroleum ether (b.p. $60-70^{\circ}$) to give 0.08 g. of unidentified material, m.p. $180.5-183^{\circ}$.

The total yield of tetraphenylsilane was 1.83 g. (30% based on lithium), while the total yield of hexaphenyldisilane was 0.86 g.

Run 3. A mixture of 10 g. (0.0385 mole) of triphenylsilane, 1.5 g. (0.217 g. atom) of lithium wire, and 50 ml. of THF was stirred between $0-5^{\circ}$ for 3.5 hours and at room temperature for 1.5 hours. The mixture was filtered and to the resulting solution was added 8.4 g. (0.008 mole) of trimethylchlorosilane in 20 ml. of THF. The mixture was stirred at

room temperature for 2.5 hours, after which work-up of the organic layer was carried out as described in the previous runs. The crude material was crystallized from 95% ethanol to give 6.18 g. (48%) of 1,1,1-trimethyl-2,2,2-triphenyldisilane, m.p. 104-106°, which showed no depression in melting point when admixed with an authentic sample.

Run 4. A mixture of 13 g. (0.05 mole) of triphenylsilane, 2.15 g. (0.31 g. atom) of lithium wire, and 60 ml. of THF was stirred at room temperature for 4 hours, after which it was treated with 12.6 g. (0.10 mole) of freshly distilled dimethyl sulfate in 20 ml. of THF. After the usual work-up of the organic layer, the crude product was distilled at 13 mm. to give 2.53 g. of dimethyl sulfate followed by two other fractions; (1) 2.09 g., b.p. 160-205°; (2) 7.23 g., b.p. 206-210°. Fraction 1, a mixture of an oil and crystals, was crystallized from 95% ethanol to give 1.38 g. of methyltriphenylsilane, m.p. 68-69°, whose melting point was not depressed when admixed with an authentic sample. This, combined with fraction 2 which crystallized on cooling and melted at 64-67°, gave a total yield of 8.61 g. (63%) of methyltriphenylsilane. Recrystallization of fraction 2 from ethanol gave 6.61 g. of product, m.p. 69-70°; total yield, 7.99 g. (58%).

The residue from the distillation was a very viscous oil from which no pure product could be isolated.

Reaction of lithium with triphenylgermane

Run 1. Five grams (0.0164 mole) of triphenylgermane, 0.14 g. (0.02 g. atom) of lithium wire, and 25 ml. of tetrahydrofuran (THF) were stirred at room temperature for 17 hours. A few minute pieces of darkly coated lithium were removed and to the resulting mixture was added 5.45 g. (0.0164 mole) of n-octadecyl bromide in 10 ml. of THF, while periodically cooling with a cold water-bath. The mixture was stirred at room temperature for 4 hours and then was hydrolyzed with water. Diethyl ether was added to the organic layer which was separated and dried over sodium sulfate. Distillation of the solvents left a white solid which was crystallized from ethanol to give 4.79 g. (53%) of material melting over the range 68-73°. Recrystallization from ethanol yielded 3.77 g. (41%) of n-octadecyltriphenylgermane, m.p. 75-77°, identified by mixed melting point.

The solvents were removed from the combined filtrates and the residual oil was distilled at 0.005 mm. to give the following fractions: (1) 0.75 g., b.p. up to 94°; (2) 0.20 g., b.p. 180-200°; (3) 1.31 g., b.p. 210-215°, n_D^{20} 1.5280, d_{20}^{20} 1.047; (4) 0.47 g., b.p. 230-240°; (5) 0.53 g., b.p. 240-245°. Fraction 2 was crystallized from ethanol to give 0.03 g. of white crystals, m.p. 128-130°. The infrared spectrum of the compound in carbon disulfide showed maxima at 3.3 μ and 9.2 μ

characteristic of aromatic C-H and phenyl-germanium bonds, respectively. No maxima characteristic of Ge-OH or Ge-O-Ge bonds were present.

Fraction 5 was crystallized from ethanol to give 0.2 g. of n-octadecyltriphenylgermane, m.p. 74-76°.

The infrared spectrum of fraction 3 showed maxima at 3.3 μ , 3.42 μ and 3.52 μ , 4.95 μ and 9.1 μ characteristic of aromatic C-H stretching, methylene C-H stretching, Ge-H stretching frequencies, and phenyl-germanium linkage, respectively. This fraction was treated successively with n-butyllithium³⁷ and n-octadecyl bromide in THF. Following the usual work-up, the crude product was distilled at 0.005 mm. to give seven fractions boiling over wide ranges, none of which could be further purified.

Run 2. A mixture of 4.0 g. (0.013 mole) of triphenylgermane, 1.15 g. (0.165 g. atom) of lithium, and 40 ml. of THF was stirred at room temperature for 2 hours, then filtered into an addition funnel, and finally was added, during 5 minutes, to a stirred solution of 4.35 g. (0.013 mole) of n-octadecyl bromide in 15 ml. of THF, while periodically cooling with a cold water-bath. Work-up as described in the previous run gave 3.15 g. (44%) of n-octadecyltriphenylgermane, m.p. 72-74°. No attempt was made to work-up the other products.

In another run employing similar conditions but a reaction time of 6 hours, the yield of n-octadecyltriphenylgermane was 41%.

Reaction of lithium with tetraphenylsilane

Eight grams (0.024 mole) of tetraphenylsilane, 0.8 g. (0.115 g. atom) of lithium wire, and 50 ml. of tetrahydrofuran (THF) were stirred at room temperature for 8.5 hours, after which the excess lithium was filtered off. To the resulting mixture was added, during 10 minutes, 5.18 g. (0.048 mole) of trimethylchlorosilane dissolved in 25 ml. of THF. Subsequently, hydrolysis was achieved with water and the organic layer was worked up as described in previous experiments. The crude product was distilled at 15 mm. to give 1.57 g. (44%) of trimethylphenylsilane, b.p. 55° , and 6.25 g. (79%) of crystalline material, m.p. $102-106^{\circ}$. Crystallization of the latter from 95% ethanol yielded 5.41 g. (69%) of 1,1,1-trimethyl-2,2,2-triphenyldisilane, m.p. $107-108^{\circ}$, identified by mixed melting point.

Reaction of phenyllithium with triphenylsilane

Seventeen milliliters of tetrahydrofuran (THF) containing 0.016 mole of phenyllithium was added to a stirred solution of 3.0 g. (0.012 mole) of triphenylsilane in 20 ml. of THF. After stirring at room temperature for 3.75 hours, the mixture was hydrolyzed with water and an insoluble solid was filtered off to give 3.31 g. of tetraphenylsilane, m.p. $233-235^{\circ}$, which

did not depress the melting point of an authentic specimen.

The organic layer was separated, dried, and the solvents were distilled to leave a solid which was crystallized from ethyl acetate to give an additional 0.39 g. of tetraphenylsilane; total yield, 3.7 g. (95%).

Reaction of phenyllithium with triphenylgermane

To a solution of 3.0 g. (0.01 mole) of triphenylgermane in 25 ml. of tetrahydrofuran (THF) was added, during 5 minutes, 12 ml. of THF containing 0.011 mole of phenyllithium. The mixture was stirred at room temperature for 1.75 hours, after which a solution of 3.33 g. (0.01 mole) of n-octadecyl bromide in 5 ml. of THF was added. After the usual work-up, the crude product was refluxed in ethanol and filtered to give a trace of insoluble material melting at 340-344°. The filtrate was concentrated and cooled to yield 4.3 g. (77%) of n-octadecyltriphenylgermane, m.p. 76-77°, which did not show any depression in melting point when admixed with an authentic sample.

Reaction of triphenylsilyllithium with triphenylsilane

Reflux temperature. The triphenylsilyllithium was prepared by stirring a mixture of 3.0 g. (0.0058 mole) of

hexaphenyldisilane, 2.0 g. (0.29 g. atom) of lithium wire, and 40 ml. of tetrahydrofuran (THF) at room temperature for 7 hours. The reaction was started as a paste and the THF was added dropwise until the addition was complete. When the cleavage was complete, as evidenced by a clear brown solution, the excess pieces of lithium were filtered off and to the resulting solution was added 3.12 g. (0.012 mole) of triphenylsilane. The mixture was refluxed for 21 hours, after which Color Test I⁴⁰ was negative. After hydrolysis with water, an insoluble product was filtered off and the organic layer from the filtrate was worked up as previously described. The residue was refluxed in petroleum ether (b.p. 28-38°) and filtered. The combined yield of slightly impure tetraphenylsilane, m.p. 227-231°, was 2.64 g. (68% based on triphenylsilyllithium). A crystallization from ethyl acetate gave 2.1 g. (54%) of pure material, m.p. 234-235°, identified by mixed melting point.

Room temperature. The triphenylsilyllithium, prepared from 3.0 g. (0.0058 mole) of hexaphenyldisilane, 0.80 g. (0.115 g. atom) of lithium, and 30 ml. of THF, was added to 6.25 g. (0.024 mole) of triphenylsilane in 15 ml. of THF. The mixture was stirred at room temperature for 6.75 hours, after which 1.00 g. of trimethylchlorosilane was added, thus resulting in a negative Color Test I⁴⁰. After hydrolysis with water, there was filtered off 0.1 g. of hexaphenyldisilane, m.p. 350-358°, identified by mixed melting point.

The solvent was distilled from the organic layer and the residue was shaken with ca. 15 ml. of petroleum ether (b.p. 28-38°). After cooling at 0°, a solid was filtered off, refluxed in 95% ethanol, and again filtered to give 0.06 g. of tetraphenylsilane, m.p. 230-232°, identified by mixed melting point. The ethanol filtrate was evaporated and the residue was crystallized from petroleum ether (b.p. 60-70°) to give 0.32 g. of triphenylsilanol, m.p. 153-155°. A mixed melting point with an authentic specimen was undepressed.

The solvent from the petroleum ether (b.p. 28-38°) filtrate was evaporated and the residue was distilled at 13 mm. to give 5.88 g. of triphenylsilane, b.p. 205-210° and a higher boiling fraction which was crystallized from 95% ethanol to yield 0.07 g. of 1,1,1-trimethyl-2,2,2-triphenyldisilane, m.p. 106-107°, identified by mixed melting point.

Reaction of triphenylsilyllithium with refluxing tetrahydrofuran

Triphenylsilyllithium, prepared from 8 g. (0.0155 mole) of hexaphenyldisilane and 2.0 g. (0.29 g. atom) of finely cut lithium wire in 75 ml. of tetrahydrofuran (THF), was refluxed for 2.7 days, after which Color Test I⁴⁰ was very faint. Most of the THF was distilled; diethyl ether was added; and the mixture was hydrolyzed with water. After filtering off

0.12 g. of hexaphenyldisilane, the organic layer was separated, dried, and the solvents were distilled under reduced pressure. The residue was refluxed briefly in petroleum ether (b.p. 28-38°) and filtered to give 2.15 g. of material, m.p. 90-104°. This was recrystallized from petroleum ether (b.p. 60-70°) to yield 1.88 g. of white needles, m.p. 107-108°. Two recrystallizations raised the melting point to 109-110°. The analysis indicated the compound to be 4-hydroxybutyltriphenylsilane.

Anal. Calcd. for $C_{22}H_{24}OSi$: C, 79.45; H, 7.28; Si, 8.46.
Found: C, 79.56, 79.42; H, 7.03, 7.28; Si, 8.65.

The infrared spectrum of the compound in carbon tetrachloride solution showed strong absorption bands at 2.75μ , 3.3μ , 3.4μ , and 9.0μ , indicative of C-OH, aromatic C-H, aliphatic C-H stretching frequencies, and phenyl-silicon linkage, respectively. There was broad band at 3.0μ .

The petroleum ether (b.p. 28-38°) filtrate was evaporated to leave a solid suspended in an oil. The solid was washed with petroleum ether (b.p. 60-70°) and then crystallized from the same solvent to give 1.95 g. of material melting over the range 80-115°, which could not be narrowed appreciably after repeated recrystallizations. The oil was distilled under reduced pressure to give 0.86 g. of material which melted over the range 85-120° after crystallization from ethanol. The residue was crystallized from petroleum ether (b.p. 60-70°) to give 0.52 g. of product, m.p. 103-105°.

Aromatic Heterocycles Containing Silicon
as the Hetero Atom⁵⁰

2,2'-Biphenylenedilithium

To a stirred suspension of 2.38 g. (0.344 g. atom) of finely cut lithium wire in 50 ml. of ether was added, during 25 minutes, a solution of 2.22 g. (0.0071 mole) of 2,2'-dibromobiphenyl in 25 ml. of ether. After stirring at room temperature for 20 minutes, the reaction mixture was refluxed for 6.5 hours. Subsequently, the excess lithium was filtered off and to the resulting solution was added 2.6 g. (0.0143 mole) of benzophenone dissolved in 20 ml. of ether. The mixture was refluxed for ca. 30 minutes and then was hydrolyzed with water. An insoluble material was filtered off and combined with additional crude product obtained after working up the organic layer in the usual manner. The combined crude product was crystallized from ethanol to give 1.68 g. (46%) of 2,2'-bis-(diphenylhydroxymethyl)-biphenyl, m.p. 254-256°; reported⁵¹ m.p. 253°.

⁵⁰One of the compounds in this section contains germanium as the hetero atom.

⁵¹A. E. Tschitschibabin and P. G. Sergejeff, Ber., 59, 654 (1926).

5,5'-Spirobi-[dibenzosilole]

Seventy-two milliliters of a solution containing 0.024 mole of 2,2'-biphenylenedilithium⁵² was added, during 1 hour, to a rapidly stirred solution of 1.87 g. (0.011 mole) of silicon tetrachloride in 30 ml. of ether. The reaction mixture was stirred at room temperature for 1.5 hours and was refluxed for 3 hours. Subsequently, 50 ml. of benzene was added and the mixture was refluxed at 46° for 2 hours. The mixture was hydrolyzed and the organic layer was worked up in the usual fashion. Most of the ether distilled and the remaining solution, on cooling, deposited 1.45 g. of product, m.p. 222-225°. The filtrate was concentrated to give an additional 0.6 g. of material; total yield, 2.05 g. (56%). Crystallization from ethanol raised the melting point of 5,5'-spirobi-[dibenzosilole] to 226-227.5°.

Anal. Calcd. for C₂₄H₁₆Si: C, 86.72; H, 4.85; Si, 8.44; mol. wt., 332. Found: C, 86.83, 86.90; H, 4.87, 5.09; Si, 8.33; mol. wt., 344, 348.

5,5'-Spirobi-[dibenzogermole]

To 185 ml. of a stirred ethereal solution containing 0.05 mole of 2,2'-biphenylenedilithium⁵² was added, during 25

⁵²H. Gilman and R. D. Gorsich, J. Am. Chem. Soc., 77, 6380 (1955).

minutes, 5.35 g. (0.025 mole) of germanium tetrachloride dissolved in 35 ml. of ether. Subsequently, the mixture was hydrolyzed with water and an insoluble solid was filtered off to give 1.7 g. of product melting over the range 230-238°. The organic layer was worked up as usual to give an additional 2.45 g. of crude product which, when combined with the ether-insoluble material and crystallized from ethyl acetate, yielded 2.15 g. of 5,5'-spirobi-[dibenzogermole], m.p. 244.5-246°. The mother liquor afforded an additional 0.62 g. of product; total yield, 2.77 g. (29%).

Anal. Calcd. for $C_{24}H_{16}Ge$: Ge, 19.23; mol. wt., 377.
Found: Ge, 18.88; mol. wt., 418, 407.

5-Chloro-5-n-dodecyldibenzosilole

Three hundred and forty-eight milliliters of an ethereal solution containing 0.1 mole of 2,2'-biphenylenedilithium⁵² was diluted to 425 ml. with additional ether and subsequently was added, during 2.5 hours, to a rapidly stirred solution of 45 g. (0.148 mole) of n-dodecyltrichlorosilane in 600 ml. of ether. When the addition was complete, the mixture was stirred at room temperature overnight, after which the ether was distilled until the distillation temperature rose to 60°. Three hundred milliliters of petroleum ether (b.p. 60-70°) was added and the mixture was refluxed for 1 hour before filtering,

while hot, in an atmosphere of nitrogen. The lithium salt was washed with several portions of petroleum ether. The solvents, together with butyl bromide, were distilled from the filtrate and the residual material was transferred to a Claisen flask. The distillation was carried out at 0.012 mm. in an electrically heated air-oven. The first fraction, 15.57 g., was collected at 93-96° and was mainly *n*-dodecyltrichlorosilane. The main fraction distilled at 180-182° to give 33.16 g. (86%) of pale yellow liquid.

Anal. Calcd. for $C_{24}H_{33}ClSi$: Cl, 9.21; Si, 7.29. Found: Cl, 8.96, 8.94; Si, 7.25, 7.27.

In four other runs the yields varied between 73 and 85%. The run yielding 73% of product also deposited 0.5 g. of 5,5'-spirobi-[dibenzosilole], m.p. 225-227°, on standing for several days. The latter was identified by a mixed melting point with an authentic specimen.

5,5-Dichlorodibenzosilole (impure)

Method A. To a rapidly stirred solution of 252 g. (1.48 moles) of silicon tetrachloride in 700 ml. of ether was added, during 3 hours, 300 ml. of an ethereal solution containing 0.078 mole of 2,2'-biphenylenedilithium⁵². After stirring the mixture overnight at room temperature, it was worked up as described in the preceding experiment. Concentration and

cooling of the filtrate resulted in the deposition of 3.5 g. of crude product which, when crystallized from ethyl acetate, afforded 2.89 g. of 5,5'-spirobi-[dibenzosilole], m.p. 227-229°, identified by mixed melting point. The remaining petroleum ether was removed and the crude product was distilled at 0.01 mm. to give a small amount of biphenyl followed by 7.41 g. (38%) of slightly impure 5,5-dichlorodibenzosilole, b.p. 108-110°, which crystallized on cooling. The material was very soluble in organic solvents which might have served as crystallization media. Sublimation did not result in any further purification.

Anal. Calcd. for $C_{12}H_8Cl_2Si$: Cl, 28.3; Si, 11.33.

Found: Cl, 26.5; Si, 10.75.

Method B (attempted). An ethereal solution containing 0.02 mole of ethylmagnesium bromide was added to a mixture of 6.16 g. (0.02 mole) of 2,2'-dibromobiphenyl and 1 g. (0.04 g. atom) of magnesium turnings ether. The mixture was refluxed for 17 hours, after which the insoluble difunctional Grignard reagent was filtered into another 3-necked flask. A solution of 3.58 g. (0.025 mole) of silicon tetrachloride in 12 ml. of ether was added and the mixture was refluxed for 4 hours. Forty milliliters of benzene was added and ether was distilled until the reflux temperature reached 70°. After refluxing at this temperature for 12 hours, an ethereal solution containing

0.18 mole of ethyllithium was added. The mixture was hydrolyzed and worked up as usual. The crude oil, on standing for a few hours, deposited 0.71 g. of 5,5'-spirobi-[dibenzosilole], m.p. 223-225°, identified by mixed melting point. No other product in the mixture was identified.

5-Benzyl-5-chlorodibenzosilole (impure)

To a stirred solution of 16 g. (0.071 mole) of benzyltrichlorosilane⁵³ in ca. 300 ml. of ether was added, during 3.75 hours, 190 ml. of an ethereal solution containing 0.05 mole of 2,2'-biphenylenedilithium⁵². The work-up was achieved in the same manner as described for 5-chloro-5-n-dodecyldibenzosilole. The crude material was distilled through a short-path Vigreux column. Two main fractions were collected; b.p. 150-160° (0.01 mm.) and b.p. 160-171° (0.01 mm.). Redistillation of the two fractions at 0.01 mm. gave 7.25 g. (47%) of impure 5-benzyl-5-chlorodibenzosilole, b.p. 150-157°.

Anal. Calcd. for $C_{19}H_{15}ClSi$: Cl, 11.6. Found: Cl, 12.3.

⁵³A. Bygden, Ber., 45, 707 (1912).

5-Chloro-5-phenyldibenzosilole

To a rapidly stirred solution of 23.45 g. (0.111 mole) of phenyltrichlorosilane in 450 ml. of ether was added, during 80 minutes, 234 ml. of an ethereal solution containing 0.07 mole of 2,2'-biphenylenedilithium⁵². Since Color Test I⁴⁰ was positive after 20 minutes, the remaining organodilithium compound was added while refluxing the reaction mixture. When the addition was complete, the mixture was worked up as described for 5-chloro-5-n-dodecyldibenzosilole. The crude product was distilled in an air-oven at 0.005 mm. to give unreacted phenyltrichlorosilane followed by 14.99 g. (73%) of pale yellow liquid which crystallized on standing for 2 days and melted over the range 69-72°. Attempts to recrystallize the product were unsuccessful due to its extreme solubility in the inert solvents tried.

Anal. Calcd. for $C_{18}H_{13}ClSi$: Cl, 12.11; Si, 9.58. Found: Cl, 11.78; Si, 9.68, 9.47.

Refluxing during the addition of the organodilithium compound seemed to be necessary, since in two runs in which the addition was achieved at room temperature the yields were 55 and 58%, and the pure compound could not be isolated.

In another run in which 25.86 g. (0.122 mole) of phenyltrichlorosilane was allowed to react with 0.08 mole of 2,2'-biphenylenedilithium⁵² in 650 ml. of ether, while refluxing,

there was obtained 1.89 g. of spirobi-[dibenzosilole], m.p. 224-226°, identified by mixed melting point. The yield of 5-chloro-5-phenyldibenzosilole was 12.87 g. (55%).

5-Chloro-5-methyldibenzosilole (impure)

An ethereal solution containing 0.065 mole of 2,2'-biphenylenedilithium⁵² was added, during 40 minutes, to a stirred refluxing solution of 19.22 g. (0.128 mole) of methyltrichlorosilane in 175 ml. of ether. When the addition was complete, the mixture was worked up as described for 5-chloro-5-n-dodecyldibenzosilole. The excess methyltrichlorosilane was distilled at atmospheric pressure and the residue was distilled at 0.007 mm. to give 12.45 g. (83%) of colorless liquid, b.p. 98-100°, which crystallized on standing, m.p. 63-68°.

Anal. Calcd. for $C_{13}H_{11}ClSi$: Si, 12.16. Found: Si, 11.18, 11.30.

The residue was crystallized from a mixture of benzene and ethanol to give 0.4 g. of 5,5'-spirobi-[dibenzosilole], m.p. 230-231°, identified by mixed melting point.

When the addition of the organodilithium compound was carried out at room temperature, the yields dropped to about 60% and the product was less pure than the material obtained when refluxing was employed.

Reaction of 2,2'-biphenylenedilithium with hexachlorodisilane

Three hundred and thirty milliliters of an ethereal solution containing 0.097 mole of 2,2'-biphenylenedilithium⁵² was added, during 1.75 hours, to a stirred solution of 11.5 g. (0.043 mole) of hexachlorodisilane in 150 ml. of ether. The mixture was worked up in a manner similar to that described for 5-chloro-5-n-dodecyldibenzosilole except for using benzene instead of petroleum ether (b.p. 60-70°). Concentration and cooling of the benzene solution yielded 2.86 g. of crystals which, when crystallized from ethyl acetate, melted at 230-231° and showed no depression in melting point when admixed with 5,5'-spirobi[dibenzosilole]. From the mother liquor was obtained an additional 1.62 g. of spiro product. Distillation of the remaining benzene left a residue which was sublimed at 130° and 17 mm. to give 1.75 g. of biphenyl, m.p. 67-69°, identified by mixed melting point. The residue was refluxed in acetone to give 7.25 g. of insoluble material which did not melt below 530°. Concentration of the acetone filtrate gave another 1.22 g. of 5,5'-spirobi-[dibenzosilole], m.p. 225-227°. The total yield of the spiro compound was 5.70 g. (20% based on hexachlorodisilane).

An ethereal solution containing 4.69 g. of the residue obtained after removal of the benzene was treated with

methyllithium. Work-up of the organic layer yielded a very viscous oil which could not be further purified.

o-Bromobenzyl bromide

A mixture of 16 g. (0.09 mole) of N-bromosuccinimide, 17.1 g. (0.10 mole) of o-bromotoluene, 0.10 g. of benzoyl peroxide, and 40 ml. of carbon tetrachloride was refluxed for 2.5 hours, after which the mixture was cooled and the succinimide was filtered off. The crude product was distilled to give 17.4 g. (77% based on N-bromosuccinimide) of product, b.p. 130-134° (18 mm.).

2,2'-Dibromobibenzyl

A solution of 16.5 g. (0.066 mole) of o-bromobenzyl bromide was added, during 20 minutes, to a stirred suspension of 0.9 g. (0.13 g. atom) of finely cut lithium wire. The mixture was stirred at room temperature for 4.5 hours and then was refluxed for 15 minutes subsequent to hydrolysis with water. The crude product, after the usual work-up of the organic layer, was distilled to give a small amount of forerun, b.p. up to 200° (18 mm.), followed by a clear liquid, b.p. 134-145° (0.06 mm.), which, after crystallization from ethanol, yielded 4.2 g.

(38%) of white plates, m.p. $82-83^{\circ}$; reported⁵⁴ m.p. 84.5° .

10,11-Dihydro-5,5-diphenyldibenzosilopin

To a stirred solution of 4.5 g. (0.026 mole) of 2,2'-dibromobibenzyl in 40 ml. of ether was added 38 ml. of an ethereal solution containing 0.52 mole of *n*-butyllithium³⁷, while cooling with an ice-bath. The mixture was stirred at room temperature for 4 hours and then was added, during 45 minutes, to a stirred solution of 6.23 g. (0.0246 mole) of diphenyldichlorosilane in 50 ml. of ether. The mixture was hydrolyzed and the organic layer was worked up in the usual manner. The residual material was washed with petroleum ether (b.p. $60-70^{\circ}$) and an insoluble substance was filtered off. This was dissolved in benzene and chromatographed on a column of alumina to give 1.36 g. (15%) of product, m.p. $170-172^{\circ}$. Recrystallization from petroleum ether (b.p. $77-115^{\circ}$) raised the melting point to $172.5-174^{\circ}$.

Anal. Calcd. for $C_{26}H_{22}Si$: C, 86.15; H, 6.12; Si, 7.74. Found: C, 86.49, 86.30; H, 6.32, 6.34; Si, 7.70.

The petroleum ether (b.p. $60-70^{\circ}$) was removed from the first filtrate and the residue was distilled under reduced

⁵⁴J. Kenner and J. Wilson, J. Chem. Soc., 1108 (1927).

pressure to give two unidentified fractions and 4.1 g. of residue which could not be further purified.

Spiro-[dibenzosilole-5,1'-silacyclohexane]

One hundred milliliters of an ethereal solution containing 0.025 mole of 2,2'-biphenylenedilithium⁵² was added, during 40 minutes, to a stirred solution of 3.38 g. (0.02 mole) of 1,1-dichlorosilacyclohexane⁸ in approximately 50 ml. of ether. As there was no evidence of reaction, benzene was added and ether was distilled until the temperature rose to 50° at which temperature the mixture was stirred for 1 hour. More ether was distilled until the temperature rose to 60°. Stirring was continued at this temperature for 16 hours. The mixture was hydrolyzed and the organic layer was worked up as described in preceding experiments. The residue, which was obtained after removal of the solvents, was dissolved in petroleum ether (b.p. 60-70°) and chromatographed on alumina. Three fractions, whose melting points ranged from 120 to 175°, were collected and sublimed at about 110° and 0.02 mm. to give 1.03 g. of sublimate melting over the range 134-140° and 0.66 g. of residue, m.p. 180-182°. The sublimate melted at 144-145.5° after two crystallizations from petroleum ether (b.p. 60-70°). The residue melted at 183-184° after crystallization from the same solvent.

Anal. Calcd. for $C_{29}H_{28}Si$ (residue); C, 86.08; H, 6.97; Si, 6.95. Found: C, 86.27; H, 6.65; Si, 7.03.

Anal. Calcd. for $C_{17}H_{18}Si$ (sublimate): C, 81.15; H, 7.24. Found: C, 81.03, 81.25; H, 7.37, 7.19.

The analyses indicated the residue to be 1,1-bis-(2-biphenyl)-silacyclohexane and the sublimate to be spiro-[dibenzosilole-5,1'-silacyclohexane].

The infrared spectra of the compounds in carbon disulfide solution were also in agreement with the assigned structures. The latter compound showed sharp bands at 8.9μ and 9.4μ , indicative of the dibenzosilole nucleus, whereas the former compound had a sharp band at 9.0μ characteristic of an aryl-silicon bond, but no band at 9.4μ .

5.5-Diethyldibenzosilole

A solution of 5.02 g. (0.032 mole) of diethyldichlorosilane in ca. 20 ml. of ether was added, during 15 minutes, to 100 ml. of a stirred refluxing ethereal solution containing 0.032 mole of 2,2'-biphenylenedilithium⁵². After refluxing for 1 hour, 90 ml. of benzene was added to the mixture and ether was distilled until the reaction temperature rose to 63° . The mixture was refluxed at this temperature for 4.5 hours and then was hydrolyzed with water. The organic layer was separated, dried, and the solvents were distilled at 15 mm. The residue

was distilled at 0.02 mm. to give one fraction, b.p. 93-95°, and a second fraction, b.p. 100-105°. The combined fractions, which crystallized on cooling, were recrystallized from a mixture of water and ethanol to give, after drying in vacuo, 1.76 g. (23%) of 5,5-diethyldibenzosilole, m.p. 60-61°.

Anal. Calcd. for $C_{16}H_{18}Si$: C, 80.63; H, 7.61. Found: C, 80.56, 80.69; H, 7.76, 7.51.

5,5-Di-n-dodecyldibenzosilole

A solution of 13.1 g. (0.03 mole) of di-n-dodecyldichlorosilane and 110 ml. of an ethereal solution containing 0.034 mole of 2,2'-biphenylenedilithium⁵² were allowed to react in a manner described in the preceding experiment. Following hydrolysis with water and work-up of the organic layer, the oily residue was distilled under reduced pressure. After collecting a small amount of forerun, there was distilled one fraction between 250-265° (0.02 mm.) and a higher boiling fraction, b.p. 315-318° (0.03 mm.), which was crystallized from ethyl acetate to give 1.05 g. of white crystals, m.p. 55-57°. The infrared spectrum of the compound in carbon disulfide solution showed a strong band at $9.5\ \mu$ indicative of a Si-O-Si linkage.

The first two fractions were redistilled to give 4.36 g. (28%) of 5,5-di-n-dodecyldibenzosilole, b.p. 240-243° (0.01 mm.), n_D^{20} 1.5246, d_{20}^{20} 0.923.

Anal. Calcd. for $C_{36}H_{58}Si$: C, 83.33; H, 11.26; MR, 171.5. Found: C, 83.17, 83.06; H, 11.46, 11.43; MR, 171.9.

5-n-Dodecyl-5-phenyldibenzosilole

Fifty milliliters of an ethereal solution containing 0.02 mole of phenyllithium⁴⁵ was slowly added to a stirred solution of 5 g. (0.013 mole) of 5-chloro-5-n-dodecyldibenzosilole in 30 ml. of ether. The mixture was stirred at room temperature overnight and then was hydrolyzed with water. The organic layer was separated, dried, and the solvent was distilled. The residue was distilled through a Vigreux column heated in an electrically wired air-oven at 0.012 mm. to give, after collecting a small amount of forerun, 4.06 g. (73%) of pale yellow liquid, b.p. 196-198°, n_D^{20} 1.5718, d_4^{20} 0.995.

Anal. Calcd. for $C_{30}H_{38}Si$: Si, 6.58; MR, 140.5. Found: Si, 6.59, 6.60; MR, 140.8.

5-(3-Biphenyl)-5-n-dodecyldibenzosilole

Ninety milliliters of an ethereal solution containing 0.017 mole of 3-biphenyllithium, prepared according to the method used for 2-biphenyllithium⁴⁷, was added, during 5 minutes, to a stirred solution of 6.0 g. (0.0155 mole) of 5-chloro-5-n-dodecyldibenzosilole in about 30 ml. of ether.

When the addition was complete, the mixture was refluxed for 1 hour, and worked up as described in the preceding run. Distillation of the solvent left a residue which was distilled at 0.008 mm. to give a small amount of forerun followed by 6.4 g. (82%) of pale yellow liquid, b.p. 242-247°, n_D^{20} 1.5992.

Anal. Calcd. for $C_{36}H_{42}Si$: Si, 5.58. Found: Si, 5.72.

5-n-Dodecyl-5-n-hexadecyldibenzosilole

The n-hexadecyllithium was prepared from 12.2 g. (0.04 mole of n-hexadecyl bromide and 1.4 g. (0.20 g. atom) of finely cut lithium wire in diethyl ether, essentially using the procedure described for n-butyllithium³⁷. The yield of organolithium compound was 0.022 mole. To this stirred solution, cooled by an ice-bath, was added, during 5 minutes, a solution of 6.0 g. (0.0155 mole) of 5-chloro-5-n-dodecyldibenzosilole in approximately 25 ml. of ether. The mixture was stirred between 0-5° for 30 minutes and at room temperature overnight. Hydrolysis was effected with water and the organic layer was worked up in the usual fashion. The residue, remaining after distillation of the solvent, was distilled at 0.005 mm. to give a forerun followed by 5.9 g. (66%) of product, b.p. 255-260°. Redistillation of the material yielded a pale yellow liquid, b.p. 232-235°, n_D^{20} 1.5170, d_4^{20} 0.918.

Anal. Calcd. for $C_{40}H_{66}Si$: C, 83.35; H, 11.57; Si, 4.88; MR, 189.9. Found: C, 83.02; H, 11.57; Si, 4.93; MR, 189.4.

5,5-Di-n-tetradecyldibenzosilole

Fifty milliliters of an ethereal solution containing 0.043 mole of n-tetradecyllithium, prepared in accordance with the procedure described for n-butyllithium³⁷, was added to a solution of 4.75 g. (0.019 mole) of impure 5,5-dichlorodibenzosilole in 50 ml. of ether. The reaction mixture was cooled by an ice-bath during the addition. When the addition was complete, the mixture was stirred at room temperature overnight and subsequently was hydrolyzed with water. The organic layer was separated, dried, and the solvent was distilled. The crude product was distilled at 0.003 mm. to give several small fractions followed by 3.95 g. (36%) of product, b.p. 245-250°, n_D^{20} 1.5170, d_4^{20} 0.914.

Anal. Calcd. for $C_{40}H_{66}Si$: Si, 4.88; MR, 189.9. Found: Si, 4.73, 4.85; MR, 190.2.

5-n-Dodecyl-5-[(methyldibenzylsilyl)-methyl]-dibenzosilole

To 80 ml. of a stirred pentane solution containing 0.02 mole of methyldibenzylsilylmethylithium, prepared from 6.43 g.

(0.0234 mole) of (chloromethyl)-methyldibenzylsilane and 3.15 g. (0.455 g. atom) of lithium ribbon, was added a solution of 6.0 g. (0.0155 mole) of 5-chloro-5-n-dodecyldibenzosilole in 20 ml. of benzene. After refluxing the mixture for 9 hours, it was hydrolyzed with water and worked up in the usual manner. The crude product was distilled through a short Vigreux column heated in an air-oven to give 2.6 g. of forerun boiling up to 238° (0.005 mm.) followed by 7.3 g. (80%) of water-clear product, b.p. $250-251^{\circ}$ (0.005 mm.), n_D^{20} 1.5750, d_4^{20} 1.005.

Anal. Calcd. for $C_{40}H_{52}Si_2$: C, 81.60, H, 5.91; Si, 9.53; MR, 192.9. Found: C, 81.60; H, 5.94; Si, 9.69, 9.52; MR, 193.7.

5,5-Dimethyldibenzosilole

An ethereal solution containing 0.068 mole of methyl-lithium was added, during 10 minutes, to a stirred solution of 15.67 g. (0.068 mole) of impure 5-chloro-5-methyldibenzosilole in about 25 ml. of ether. The reaction mixture was stirred at room temperature overnight and was worked up in the usual fashion. The crude product was crystallized from methanol to give 9.93 g. (70%) of colorless plates, m.p. $58-59^{\circ}$. The analytical sample melted at $60-61^{\circ}$.

Anal. Calcd. for $C_{14}H_{14}Si$: C, 79.93; H, 6.72. Found: C, 80.30, 80.45; H, 6.64, 6.66.

5-Benzyl dibenzosilole

A solution of 6.46 g. (0.021 mole) of 5-benzyl-5-chloro-dibenzosilole in 20 ml. of ether was added, during 10 minutes, to a stirred suspension of 0.76 g. (0.02 mole) of lithium aluminum hydride in approximately 50 ml. of ether. The mixture was refluxed for 12 hours and then was filtered in a nitrogen atmosphere. Most of the ether was distilled and replaced with petroleum ether (b.p. 60-70°). Again, the mixture was filtered in a nitrogen atmosphere and the petroleum ether distilled from the filtrate. The residue was distilled through a short-path Vigreux column at 0.005 mm. to give 4.07 g. (72%) of colorless liquid, b.p. 135-138°, which crystallized on standing for 2 hours. The distillate was crystallized from ethanol to give white needles, m.p. 68.5-69.5°.

Anal. Calcd. for $C_{19}H_{16}Si$: C, 83.77; H, 5.92; Si, 10.30. Found: C, 83.72, 83.50; H, 6.01, 6.23; Si, 10.12.

5-Phenyl dibenzosilole (impure)

To a stirred suspension of 1.6 g. (0.042 mole) of lithium aluminum hydride in 140 ml. of ether was added, during 30 minutes, a solution of 11.1 g. (0.038 mole) of 5-chloro-5-phenyl dibenzosilole in 70 ml. of ether. When the addition was complete, the mixture was refluxed for 23 hours, after which

the work-up was carried out as described in the preceding experiment. The crude product was distilled at 0.005 mm. to give 8.63 g. (88%) of colorless liquid, b.p. 130-131°, which crystallized on standing for several hours. Crystallization from methanol gave a product melting at 58-60°.

Anal. Calcd. for $C_{18}H_{14}Si$: Si, 10.85. Found: Si, 10.02, 10.59.

5,5-Diphenyldibenzosilole

Method A. A mixture of 1 g. (0.0039 mole) of 5-phenyldibenzosilole in 25 ml. of ether and 10 ml. of an ethereal solution containing 0.005 mole of phenyllithium was stirred at room temperature for 30 minutes. The mixture was hydrolyzed with water and the organic layer was worked up as described previously. Distillation of the solvent left a solid melting over the range 109-140°. The material was crystallized from ethanol to yield 0.98 g. of product, m.p. 148-149°. From the mother liquor was obtained an additional 0.05 g. of 5,5-diphenyldibenzosilole; total yield, 1.05 g. (81%). A mixed melting point with an authentic sample⁵² prepared from diphenyldichlorosilane and 2,2'-biphenylenedilithium showed no depression. Also, the infrared spectra were identical.

Method B. A solution of 1.35 g. (0.0046 mole) of 5-chloro-5-phenyldibenzosilole in 25 ml. of ether was allowed

to react with 0.008 mole of phenyllithium in the same manner as described in the preceding experiment. The crude product, after the usual work-up, was crystallized from ethanol to give 1.1 g. (72%) of 5,5-diphenyldibenzosilole, m.p. 147-148°, identified by mixed melting point.

Method C. To 1.23 g. (0.0049 mole) of impure 5,5-dichlorodibenzosilole dissolved in 20 ml. of ether was added 18 ml. of a 0.87 M phenyllithium solution. After refluxing the mixture for 45 minutes, it was hydrolyzed and worked up as described in the preceding runs to yield 1.21 g. (74%) of 5,5-diphenyldibenzosilole, m.p. 148-149°.

5,5'-Dimethyl-5,5'-bi-[dibenzosilole]

A mixture of 9.16 g. (0.0396 mole) of 5-chloro-5-methyldibenzosilole, 0.99 g. (0.043 g. atom) of sodium, and 100 ml. of xylene was refluxed for 25 hours, after which ethanol was added to the purple mixture until the evolution of hydrogen ceased. The mixture was hydrolyzed with water. The organic layer was separated, combined with two ether extracts of the aqueous layer, and dried over sodium sulfate. Distillation of the solvents left a residue which was crystallized from ethanol to give 3.3 g. (43%) of product, m.p. 180-182°. Recrystallization from ethanol raised the melting point to 185-186°.

Anal. Calcd. for $C_{26}H_{22}Si_2$: C, 79.97; H, 5.68; Si, 14.37. Found: C, 80.29; H, 5.73; Si, 14.21.

Concentration of the filtrate from the first crystallization deposited a solid which was crystallized from ethanol to give 1.05 g. of material melting over the range 107-119°. Two additional crystallizations did not improve the melting range. The infrared spectrum of the material in carbon disulfide solution was very similar to that of 5,5'-oxybis-[5-methyldibenzosilole].

5,5'-Di-n-dodecyl-5,5'-bi-[dibenzosilole]

A mixture of 5 g. (0.013 mole) of 5-chloro-5-n-dodecyl-dibenzosilole, 0.30 g. (0.013 g. atom) of sodium, and ca. 80 ml. of xylene was refluxed for 19 hours, after which the mixture was worked up in the same manner described in the preceding preparation. After distilling the solvents, the residue was crystallized successively from a mixture of petroleum ether (b.p. 28-38°) and ethanol and from a mixture of ethanol and ethyl acetate to yield 2.42 g. (53%) of material, m.p. 59-61°.

Anal. Calcd. for $C_{48}H_{66}Si_2$: C, 82.41; H, 9.52; Si, 8.03. Found: C, 82.75; H, 9.37; Si, 8.03, 8.09.

The infrared spectrum showed no band at 9.5μ characteristic of a Si-O-Si linkage.

5,5'-Diphenyl-5,5'-bi-[dibenzosilole] (attempted)

One hundred milliliters of xylene, 3.98 g. (0.0135 mole) of 5-chloro-5-phenyldibenzosilole, and 0.5 g. (0.022 g. atom) of sodium were refluxed for 21 hours without any color change being observed. The excess sodium was destroyed with ethanol. Work-up and hydrolysis of the reaction mixture was carried out as described previously. The residue was washed with petroleum ether (b.p. 28-38°) and the insoluble product was crystallized twice from ethyl acetate to give 1.52 g. (21%) of material, m.p. 203-204°. The infrared spectrum of the compound in carbon disulfide solution showed an absorption band at 9.5 μ , indicating the material to be 5,5'-oxybis-[5-phenyldibenzosilole].

Anal. Calcd. for $C_{36}H_{26}OSi_2$: Si, 10.57. Found: Si, 10.60, 10.57.

5-Hydroxy-5-methyldibenzosilole (attempted)

Two grams (0.0087 mole) of impure 5-chloro-5-methyldibenzosilole dissolved in about 20 ml. of diethyl ether was neutralized with ca. 0.2 N sodium hydroxide, while cooling the ethereal solution with an ice-bath. The organic layer was separated, dried over sodium sulfate, and the ether distilled at 14 mm., while keeping the distillation temperature below 20°. The residue was washed with petroleum ether (b.p. 28-38°) and

filtered to give 1.16 g. (63%) of product, m.p. 153-157°. One crystallization from a mixture of acetone and water raised the melting point to 157-158°.

Although the infrared spectrum of the compound in carbon disulfide solution showed a sharp peak at 2.7μ , indicative of a Si-OH bond, and no broad band at 9.6μ , characteristic of a Si-O-Si linkage, the carbon, hydrogen, and silicon analyses indicated the material to be the disiloxane.

5,5'-Oxybis-[5-methyldibenzosilole]

An ethereal solution of 2.69 g. (0.0115 mole) of impure 5-chloro-5-methyldibenzosilole in about 100 ml. of ether was neutralized with sodium hydroxide. The organic layer was separated, dried, and the solvent was evaporated leaving a crystalline material which was allowed to stand in a mixture of methanol and water for 6 weeks. Filtration and drying of the resulting crystals gave 1.8 g. (77%) of product, m.p. 125-127°. Recrystallization from a mixture of chloroform and methanol raised the melting point to 127-128°.

Anal. Calcd. for $C_{26}H_{22}OSi$: C, 76.85; H, 5.48. Found: C, 77.12; H, 5.69.

5,5'-Oxybis-[5-n-dodecyldibenzosilole]

Run 1. To 3 g. (0.0078 mole) of 5-chloro-5-n-dodecyldi-benzosilole in ca. 25 ml. of ether was added 0.05 N sodium hydroxide solution until the mixture was definitely basic. The organic layer was separated, dried over sodium sulfate, and the ether distilled on a steam-bath. The residue was distilled through a short-path Vigreux column at 0.003 mm. to give four fractions which boiled between 190-200°. The first 3 fractions, 1.21 g., crystallized on standing for about 1 week. The last fraction, 0.77 g., contained some crystalline material after standing for several weeks. The combined crystalline material was recrystallized from ethanol to give 1.28 g. (46%) of colorless needles, m.p. 74-75°.

Anal. Calcd. for $C_{48}H_{66}OSi_2$: C, 80.62; H, 9.30. Found: C, 80.97, 80.75; H, 9.30, 9.42.

The infrared spectrum of the compound in carbon disulfide solution showed a broad absorption band at $9.6\ \mu$ characteristic of a Si-O-Si linkage.

Run 2. A mixture of water and 2.53 g. (0.0066 mole) of 5-chloro-5-n-dodecyldibenzosilole was allowed to stand for 3 weeks. The organic material was extracted with ether. The ethereal solution was worked up in the manner described in run 1. The crude product was refluxed in ethanol. After decanting the solution from a small amount of oil, the ethanolic

solution was allowed to stand in a refrigerator for about 3 days, after which there was deposited 1.14 g. (48%) of product, m.p. 73-75°. The material proved to be identical with that from run 1 by mixed melting point and infrared spectrum.

Reaction of formic acid with 5,5-diphenyldibenzosilole

A mixture of 1.0 g. (0.003 mole) of 5,5-diphenyldibenzosilole and 50 ml. of 98% formic acid was refluxed for 22 hours. The formic acid was distilled and the residue was sublimed in vacuo to give 0.16 g. (35%) of biphenyl. The remaining material could not be further purified.

Reaction of 2,2'-biphenylenedilithium with 5-chloro-5-methyldibenzosilole

Two grams (0.0087 mole) of impure 5-chloro-5-methyldibenzosilole and 30 ml. of an ethereal solution containing 0.009 mole of 2,2'-biphenylenedilithium⁵² was stirred at room temperature for 29 hours, after which the mixture was poured onto a mixture of Dry Ice and diethyl ether. The organic layer was separated, extracted once with 5% sodium hydroxide, and dried over sodium sulfate. The solvent was distilled; the residue was washed with petroleum ether (b.p. 28-38°); and the granular material was filtered off to give 1.08 g. (38%) of 5,5'-

spirobi-[dibenzosilole], m.p. 225-227°, whose melting point was undepressed when admixed with an authentic sample.

Distillation of the solvent from the filtrate left an oil which was distilled at 0.005 mm. to give 0.15 g. of forerun followed by 0.65 g. (36%) of 5,5-dimethyldibenzosilole which was crystallized from methanol to give 0.32 g. (18%) of white plates, m.p. 59-61°. A mixed melting point with an authentic sample was undepressed.

Reaction of 2,2'-biphenylenedilithium with triethylchlorosilane
(attempted)

A solution of 4.18 g. (0.028 mole) of triethylchlorosilane and 0.018 mole of 2,2'-biphenylenedilithium⁵² was refluxed for 4 hours. Benzene was added to the mixture and refluxing was continued at 55° for 12 hours and then at 60° for 6 hours. Color Test I⁴⁰ was positive. The mixture was hydrolyzed with water and 0.75 g. of a product, insoluble in the common organic solvents, was filtered off. Distillation of the residue, after evaporation of the solvent from the organic layer, gave 1.2 g. of forerun followed by 1.5 g. of unidentified liquid, b.p. 130-150° (0.022 mm.).

5-(2-Biphenyl)-5-phenyldibenzosilole

From 5,5'-spirobi-[dibenzosilole] and phenyllithium. A tetrahydrofuran (THF) solution containing 0.015 mole of phenyllithium was allowed to interact with a solution of 2 g. (0.006 mole) of 5,5'-spirobi-[dibenzosilole] in 20 ml. of THF. After stirring the mixture at room temperature for 6 hours, Color Test I⁴⁰ was negative. Following hydrolysis and work-up of the organic layer, there remained an oil which was refluxed in ethanol. An insoluble material was filtered off to give 1.26 g. (51%) of 5-(2-biphenyl)-5-phenyldibenzosilole, m.p. 137-138°. A recrystallization from petroleum ether (b.p. 60-70°) did not change the melting point.

Anal. Calcd. for $C_{30}H_{22}Si$: C, 87.77; H, 5.40; Si, 6.84. Found: C, 87.82; H, 5.79; Si, 6.90.

From 5-chloro-5-phenyldibenzosilole and 2-biphenyllithium. A mixture of 2.3 g. (0.0078 mole) of 5-chloro-5-phenyldibenzosilole and 35 ml. of an ethereal solution containing 0.009 mole of 2-biphenyllithium⁵² was stirred at room temperature for 15 minutes and refluxed for 45 minutes. The mixture was hydrolyzed with water. The organic layer was separated, dried, and the ether distilled. The residue was taken up in benzene and chromatographed on alumina. Distillation of the solvent from the eluates left a white powder which was sublimed in vacuo to give 0.3 g. of biphenyl, m.p. 65-67°.

The residue was crystallized from petroleum ether (b.p. 60-70°) to give 1.17 g. of clear prisms, m.p. 137-138°, which showed no depression in melting point when admixed with the material obtained in the preceding experiment. Concentration and cooling of the filtrate yielded an additional 0.46 g. of product, m.p. 134-136°; total yield, 1.63 g. (51%).

Reaction of lithium with 5,5-dimethyldibenzosilole

A mixture of 3.1 g. (0.0148 mole) of 5,5-dimethyldibenzosilole, 0.54 g. (0.072 g. atom) of finely cut lithium wire, and 30 ml. of diethyl ether was stirred at room temperature for 15 minutes without any sign of reaction. Approximately 5 ml. of tetrahydrofuran was added and, after a few minutes, the mixture became dark green and showed a positive Color Test I⁴⁰. The mixture was stirred at room temperature for 4.3 hours and then was hydrolyzed with water. The organic layer was separated and worked up in the usual manner. The residue was crystallized from methanol to give 1.60 g. of 5,5-dimethyldibenzosilole, m.p. 55-57°, identified by mixed melting point and infrared spectrum. The solvent was evaporated from the filtrate and the residue was sublimed in vacuo to give an additional 0.35 g. of 5,5-dimethyldibenzosilole, m.p. 53-55°; total yield, 1.85 g. (60%). The reduction product, the 1,4-dihydro derivative, was looked for but not detected.

Reaction of lithium with 5,5'-dimethyl-5,5'-bi-[dibenzosilole]

Two grams (0.0051 mole) of 5,5'-dimethyl-5,5'-bi-[dibenzosilole], 1.15 g. (0.166 g. atom) of lithium wire, and 30 ml. of tetrahydrofuran were stirred at room temperature for 4 hours, after which the excess lithium was filtered off. To the resulting green mixture was added 1.5 g. (0.012 mole) of freshly distilled dimethyl sulfate in 10 ml. of THF. The mixture was hydrolyzed with water, diethyl ether was added, and the organic layer was worked up in the usual manner. The crude product was distilled at 0.005 mm. to give 0.2 g. of forerun followed by 1.15 g. (54%) of 5,5-dimethyldibenzosilole, b.p. 87°, which crystallized on cooling and melted at 55-57°. A mixed melting point with an authentic sample showed no depression.

DISCUSSION

Noncyclic Organosilicon Compounds

Closely related to the search for thermally stable organosilicon compounds has been the concomitant problem of having these compounds possess wide liquid ranges. The latter obstacle is best overcome by introducing a maximum of asymmetry into the molecule. The former problem is closely related to the molecular weight as well as to the basic structure of the molecule. Initial efforts to surmount this over-all problem have been directed toward the screening of a number of alkyl and/or aryl substituted organosilicon compounds for the purpose of qualitatively evaluating the effects of various organic groupings on the physical properties of the molecules.

Miles⁵⁵ observed that some long-chained alkyl substituted organosilicon compounds were promising both with respect to boiling points and melting points. At elevated temperatures and in the presence of oxygen, however, these types are more prone to oxidation than aryl substituted organosilicon compounds. Moreover, the aromatic types are more resistant to radiation than the compounds containing alkyl groups.

⁵⁵D. Miles, Unpublished Ph.D. Thesis, Iowa State College Library, Ames, Iowa (1957).

Goodman¹ found that molecules containing the p-phenoxyphenyl, m-trifluoromethylphenyl, and m-tolyl groups possessed excellent thermal stabilities but unless the molecules had at least one long-chained alkyl group, the compounds inherently had high melting points.

In these studies, some m-halophenyl substituted organosilicon compounds were screened partly because of some of Goodman's promising results and partly because Gainer⁵⁶ noted that the lubricity of certain silicones was improved by incorporating in the molecules substituted phenyl groups in which the substituents were halogens or halogen-containing groups.

In Table 3, the screening data are recorded for the various m-halophenyl substituted organosilicon compounds. These data were obtained by inserting the compound to be studied in a capillary tube which was heated in a copper block by means of a Bunsen burner. A 500°-thermometer was used to measure the temperature. The volatilization point or range was that temperature at which either all of the liquid disappeared from the bottom of the capillary tube or that temperature at which rapid refluxing was observed in the top of the tube.

It is evident, at least on the basis of the compounds containing m-fluorophenyl and phenyl groups, that the m-fluorophenyl group shows little tendency to contribute to a melting

⁵⁶G. C. Gainer, Ind. Eng. Chem., 46, 2355 (1954).

Table 3. Thermal stabilities of m-halophenylsilanes^a

Compound	M.p., °C	Thermal stability, °C
Tetrakis-(<u>m</u> -fluorophenyl)silane	196-197	vol. 400
Tetrakis-(<u>m</u> -fluorophenyl)germane	194-195	vol. 400
Tris-(<u>m</u> -fluorophenyl)-phenylsilane	191.5-193	vol. 400
Bis-(<u>m</u> -fluorophenyl)-diphenylsilane	195-196	vol. 400-410
<u>m</u> -Fluorophenyltri-phenylsilane	208-209	vol. 410-415
Tetrakis-(<u>m</u> -chlorophenyl)-silane	148-149	vol. 460
Tris-(<u>m</u> -chlorophenyl)-phenylsilane	87.5-89	vol. 460
Bis-(<u>m</u> -chlorophenyl)-diphenylsilane	110-111	vol. 445-450
<u>m</u> -Chlorophenyltri-phenylsilane	157-158	vol. 450; trace of dk. residue
<u>n</u> -Dodecyltris-(<u>m</u> -fluorophenyl)-silane	35-37	vol. 410-420 (dec.)
Tris-(<u>m</u> -fluorophenyl)- <u>n</u> -hexadecylsilane	36-38	vol. 410-420 (dec.)
Tris-(<u>m</u> -fluorophenyl)- <u>n</u> -octadecylsilane	38-40	vol. 410-420 (dec.)

^aOne organogermanium compound is included.

point lowering. This is in sharp contrast to the analogous m-chlorophenyl derivatives which have higher volatilization temperatures and show pronounced fluctuations in melting points. These differences are probably due to the smaller covalent radius of fluorine as compared to chlorine.

The o-halophenyl substituted organosilicon compounds were unavailable for examination because of the instability of the intermediate o-halophenyllithium compounds necessary for the synthesis of such types⁵⁷. Although both o-fluorophenyl-⁵⁸ and o-chlorophenylmagnesium bromide⁵⁹ have been synthesized, they were not used for preparative purposes, since a previous attempt to couple the latter Grignard reagent with trimethylchlorosilane failed, presumably because of steric hindrance.

In Table 4, compounds having either a $R_3SiCH_2CH_2SiR_3$ or a $R_3SiC_6H_4SiR_3$ skeleton, are listed. The two most promising compounds are p- and m-phenylenebis-[tri-n-decylsilane], both of which are liquids and volatilize at about 450° . It is also evident in those compounds in which R is alkyl that as the length of the alkyl group increases there is a corresponding increase in melting point. Nevertheless, it is noteworthy that

⁵⁷H. Gilman and R. D. Gorsich, J. Am. Chem. Soc., 78, 2217 (1956).

⁵⁸G. E. Hall, R. Piccolini and J. D. Roberts, ibid., 77, 4540 (1955).

⁵⁹H. A. Clark, A. F. Gordon, C. W. Young, and M. J. Hunter, 73, ibid., 3798 (1951).

Table 4. Thermal stabilities of organosilicon compounds of the type $R_3SiCH_2CH_2SiR_3$ and $R_3SiC_6H_4SiR_3$

Compound	M.p., °C	Thermal stability, °C
1,2-Ethylenebis-[tri-benzylsilane]	136-137	vol. 470-480 (yellow); dk. orange residue
1,2-Ethylenebis-[tri-2-ethylhexylsilane]	215-220/0.04 ^a	vol. 425-435
1,2-Ethylenebis-[tri-n-hexadecylsilane]	45-48	vol. 480-490 (yellow)
m-Phenylenebis-[tri-benzylsilane]	155-157	vol. 505-515 (yellow); trace of orange residue
m-Phenylenebis-[tri-n-decylsilane]	285-288/0.03 ^a	vol. 440-450
p-Phenylenebis-[tri-n-decylsilane]	290-294/0.07 ^a	vol. 440-450

^aB.p., °C/mm.

1,2-ethylenebis-[tri-n-hexadecylsilane], a compound with a molecular weight of approximately 1500, melts at 48° and volatilizes at about 490°. This is the highest molecular weight compound prepared by this writer.

A route to compounds of the type $R_3Si(CH_2)_nSiR_3$ was by the addition of an R_3SiH compound to an olefinic linkage⁴². More specifically, triphenylsilane was added to 4-pentenyltriphenylsilane using benzoyl peroxide as the initiator to give 1,5-pentamethylenebis-[triphenylsilane]. This compound was also

prepared from 1,5-pentamethylenedilithium and triphenylchlorosilane.

Organosilylmethylolithium Compounds

The introduction of a high molecular weight, unsymmetrical organosilicon grouping into a molecule can be accomplished via an organosilicon compound containing a chloromethyl radical by converting the carbon-chlorine bond into a carbon-lithium bond with lithium metal. Trimethylsilylmethylolithium⁶⁰ and trimethylsilylmethylmagnesium chloride⁶¹ were prepared in good yields from the reaction of (chloromethyl)-trimethylsilane with lithium and magnesium, respectively, and have proven to be very versatile intermediates for the preparation of other carbon-functional compounds. However, no R_3SiCH_2Li compounds have been reported in which two of the R groups are phenyl or benzyl.

(Chloromethyl)-methyldibenzylsilane and (chloromethyl)-methyldiphenylsilane were synthesized by allowing (chloromethyl)-methyldichlorosilane to interact with benzylmagnesium chloride and phenyllithium, respectively. This same type of

⁶⁰L. H. Sommer, R. M. Murch, and F. A. Mitch, ibid., 76, 1619 (1954).

⁶¹F. C. Whitmore and L. H. Sommer, ibid., 68, 481 (1946).

reaction could not be applied to the synthesis of (chloromethyl)-di-n-dodecylmethylsilane or (chloromethyl)-di-n-tetradecylmethylsilane. Apparently an alkyl lithium compound, in this case n-dodecyl lithium, being a strong base, reacts with the chloromethyl-silicon linkage, most likely via scission of the silicon-carbon bond. n-Tetradecylmagnesium bromide also gave negative results when attempts were made to prepare the tetradecyl derivative. In this case, stringent conditions were used to force the reaction, the consequence of which could well have led to cleavage of the chloromethyl-silicon linkage, even though the Grignard reagent is a weaker base than n-dodecyl lithium. This cleavage of the carbon-silicon bond in such types is not unexpected, since (chloromethyl)-trimethylsilane has been cleaved by such strong bases as potassium hydroxide in moist butanol⁶² and sodium amide in liquid ammonia.⁶³

(Chloromethyl)-methyldibenzylsilane reacted smoothly with lithium ribbon in refluxing n-pentane to give, after treatment of the reaction mixture with benzophenone, [(methyldibenzylsilyl)-methyl]-diphenylmethanol in a good yield. On the other hand, (chloromethyl)-methyldiphenylsilane did not react with lithium in n-pentane, but the reaction did proceed in refluxing benzene. It appears, on the basis of these two reactions,

⁶²G. F. Roedel, *ibid.*, 71, 269 (1949).

⁶³J. E. Noll, B. F. Daubert, and J. L. Speier, *ibid.*, 73, 3781 (1951).

that the ease of formation of a R_3SiCH_2Li compound decreases as the number of R groups which are aryl increases. If this trend is continuous, then it might be expected that (chloromethyl)-triphenylsilane would react only with difficulty, if at all, with lithium in refluxing benzene.

Metalation Reactions

An extremely useful method for preparing organolithium compounds is by a metalation reaction wherein a hydrogen ortho to a substituent having an unshared electron pair is replaced by an alkali metal atom of a metalating agent such as n-butyllithium. There is a difference of opinion on the mechanism of the metalation reaction which has been reviewed recently by Gilman and Morton⁶⁴. Morton⁶⁵ has stressed the importance of the metallic cation and has visualized the mechanism as involving an electrophilic attack of the cation on the carbon atom, the removal of the proton being of secondary importance. Recent evidence seems to support the view of Roberts and Curtin⁶⁶ who proposed that the metallic atom first coordinates

⁶⁴H. Gilman and J. A. Morton, Jr. in R. Adams, "Organic Reactions," John Wiley and Sons, New York, N. Y., 1954, Vol. 8, p. 258.

⁶⁵A. A. Morton, J. Am. Chem. Soc., 69, 969 (1947).

⁶⁶J. D. Roberts and D. Y. Curtin, ibid., 68, 1658 (1946).

with the unshared electron pair of the substituent, or in the case of heterocyclic aromatic compounds with the unshared electrons of the hetero atom. They also stated that following the initial coordination, the most acidic hydrogen is removed by a nucleophilic attack of the carbanion from the metalating agent. Furthermore, the initial coordination should facilitate attack on the ortho position.

Strongly supporting the latter mechanism is the fact that metalation occurs preferentially at the position ortho to the hetero atom. Moreover, Gronowitz and Halvarson⁶⁷ have demonstrated that there is a pronounced isotope effect for the metalation of thiophene containing tracer amounts of thiophene-2-t with n-butyllithium, implying that abstraction of hydrogen is the rate determining step.

In view of the latter mechanism and assuming that the catalytic effect of ethers on the metalation reaction depends on their ability to coordinate the metalating agent and thus facilitate polarization of the carbon-metal bond, it was thought that tetrahydrofuran should be able to solvate the cation more effectively than diethyl ether, and, consequently, enhance the polarization of the carbon-metal bond. This supposition was based, in part, on some studies of Brown and

⁶⁷S. Gronowitz and K. Halvarson, Arkiv For Kemi, 8, 343 (1955).

Adams⁶⁸ who have shown that tetrahydrofuran is more basic toward boron trifluoride than is diethyl ether. This difference has been ascribed to steric strains resulting from spatial limitations within the respective molecules.

The metalation of dibenzofuran by *n*-butyllithium was found to be markedly enhanced when carried out in a mixture of tetrahydrofuran and diethyl ether. In fact, the metalation proceeded in higher yields under conditions milder than ever described previously⁶⁹. This method of metalation was extended to furan and dibenzothiophene in these studies. Furan was metalated in a mixture of tetrahydrofuran and diethyl ether at -30° by *n*-butyllithium to give, after carbonation, 75% of 2-furoic acid, while the metalation of dibenzothiophene in only tetrahydrofuran at room temperature afforded 62% of 4-dibenzothiophenecarboxylic acid after carbonation of the metalated product. The ability of tetrahydrofuran to facilitate metalation is emphasized in the latter reaction, for it has been observed recently that the metalation of dibenzothiophene in a mixture of tetrahydrofuran and diethyl ether gives a considerably lower yield of 4-dibenzothiophenecarboxylic acid when employing similar reaction conditions⁷⁰.

⁶⁸H. C. Brown and R. M. Adams, J. Am. Chem. Soc., **64**, 2557 (1957).

⁶⁹H. Gilman and R. D. Gorsich, J. Org. Chem., **22**, In press (1957).

⁷⁰Suzanne Gray, Chemistry Dept., Iowa State College, Ames, Iowa, Information on metalation reactions, Private communication (1957).

Cleavage of a Carbon-Carbon Bond by Lithium

9,9-Diphenylfluorene underwent almost a quantitative cleavage in 15 hours by lithium in tetrahydrofuran to give, after hydrolysis of the reaction mixture, 9-phenylfluorene. This reaction is not novel since Koelsch⁷⁴ found that stirring 9-benzyl-9-phenylfluorene with sodium amalgam in diethyl ether for 5 days afforded, after hydrolysis, 40% of 9-phenylfluorene, but it does emphasize that tetrahydrofuran has a pronounced effect on facilitating the cleavage.

Cleavage Reactions of Some Noncyclic

Organosilicon Compounds

Incidental to the cleavage studies of some dibenzosilole compounds by lithium in tetrahydrofuran, which reactions will be described in the next section, it was decided to reinvestigate the alkali metal cleavages of some related noncyclic compounds, namely, triphenylsilane and diphenylsilane, in an attempt to learn more of the mechanism of the reaction.

Benkeser et al.⁷⁵ observed that triphenylsilane was cleaved by sodium-potassium alloy in diethyl ether to yield

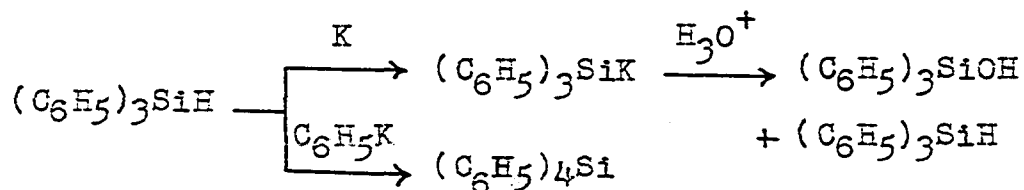
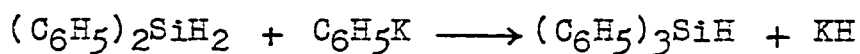
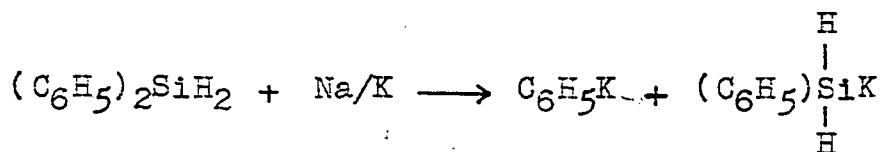
⁷⁴C. F. Koelsch, J. Am. Chem. Soc., 56, 1605 (1934).

⁷⁵R. A. Benkeser, H. Landesman, and D. J. Foster, ibid., 74, 648 (1952).

1,1,1-trimethyl-2,2,2-triphenyldisilane after treatment of the reaction mixture with trimethylchlorosilane. When diphenylsilane was cleaved by the alloy under similar conditions, only tetraphenylsilane was isolated. In the first study, no reaction route was proposed for either reaction, but in a later publication Benkeser and Foster⁷⁶ examined the reaction more closely and concluded that the mechanism of the cleavage of triphenylsilane proceeded by a reaction path different from that of diphenylsilane, since the latter formed tetraphenylsilane when treated with sodium-potassium alloy without the subsequent addition of bromobenzene, while the former did not form tetraphenylsilane from triphenylsilane and alloy unless bromobenzene was added to the reaction mixture. It was further shown that after triphenylsilylpotassium formed, there was little tendency, if any, for one or more of the phenyl groups to be lost by cleavage. When only one or two phenyl groups were attached to silicon, however, the cleavage of one or both of the groups occurred readily.

On the basis of the aforementioned evidence, the mechanism of the diphenylsilane cleavage was rationalized by invoking phenylpotassium or phenylsodium as an intermediate. The reaction scheme is illustrated below.

⁷⁶R. A. Benkeser and D. J. Foster, *ibid.*, 74, 4200 (1952).



No explanation was advanced to account for the formation of triphenylsilylpotassium from triphenylsilane and sodium-potassium alloy, although, in some related work, Benkeser and Foster⁷⁷ postulated phenylsodium as being an intermediate in the cleavage of triphenylsilane by sodium metal at elevated temperatures in hydrocarbon solvents. In this reaction, the phenylsodium was assumed to originate from the cleavage of triphenylsilane by sodium and that tetraphenylsilane was then formed by the reaction of phenylsodium with triphenylsilane.

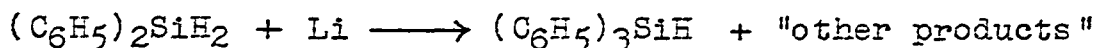
If the silicon-hydrogen bond of triphenylsilane were not being cleaved by sodium-potassium alloy, it seems reasonable to assume that tetraphenylsilane could be an intermediate in this cleavage reaction and, as has been demonstrated by Gilman

⁷⁷R. A. Benkeser and D. J. Foster, ibid., 74, 5314 (1952).

and Wu⁷⁸, it would be cleaved by excess alloy to give triphenylsilylpotassium and phenylpotassium which is unstable in diethyl ether. Tetraphenylsilane may not have been observed in the reaction of triphenylsilane with sodium-potassium alloy, because the amount of alloy employed was sufficient to cleave any tetraphenylsilane which may have been produced.

In order to substantiate or refute this view, it was decided to reinvestigate the cleavage of triphenylsilane as well as that of diphenylsilane by employing the less reactive alkali metal, lithium, and tetrahydrofuran as the solvent.

The cleavage of diphenylsilane by lithium in tetrahydrofuran yielded triphenylsilane in such an amount as to imply that only one phenyl group was cleaved.



This may be due to the lesser reactivity of lithium as a cleaving agent or it is equally possible, if not more likely, that the darkly coated pieces of lithium were incapable of further reaction with a compound having a silicon-hydrogen bond.

The cleavage of triphenylsilane proved to be much more complex and an attempt will be made to interpret the results of these reactions after enumerating the following facts:

⁷⁸H. Gilman and T. C. Wu, J. Org. Chem., 18, 753 (1953).

1. When triphenylsilane was treated with an excess of lithium metal in tetrahydrofuran and then derivatized with dimethyl sulfate, 63% of methyltriphenylsilane was obtained. No other pure product was isolated and in no run was there any evidence for the presence of phenyllithium.
2. Approximately the same amounts of tetraphenylsilane and triphenylsilyllithium, isolated as 1,1,1-trimethyl-2,2,2-triphenyldisilane, were obtained when one mole of triphenylsilane was allowed to react with slightly more than one gram atom of lithium metal. When the amount of triphenylsilane was doubled, the yield of tetraphenylsilane was approximately the same as that found in the reaction utilizing about a 1:1 molar ratio of reactants, but no 1,1,1-trimethyl-2,2,2-triphenyldisilane was found after treating the reaction mixture with trimethylchlorosilane. Instead, a small amount of hexaphenyldisilane was isolated.
3. The cleavage of tri-2-biphenylsilane by lithium yielded, after hydrolysis of the reaction mixture, an amount of biphenyl which indicated the scission of two biphenyl groups.
4. Tetraphenylsilane was cleaved by lithium in tetrahydrofuran to yield both trimethylphenylsilane and 1,1,1-trimethyl-2,2,2-triphenyldisilane, subsequent

to treatment of the reaction mixture with trimethylchlorosilane.

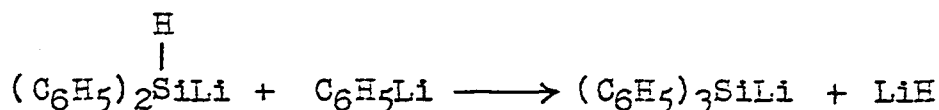
5. No evidence was found in any of the reactions to indicate the presence of a species like $(C_6H_5)_2SiLiH$ or any other similar silicon-containing cleavage fragment.

On the basis of these findings, it can be concluded that tetraphenylsilane is an intermediate, though possibly not the only one leading to the formation of triphenylsilyllithium.

It is also evident from these data that a reaction involving the cleavage of only one phenyl group from a triphenylsilane molecule is untenable since, if this were true, only 50% of triphenylsilyllithium would be formed. To account for a yield of triphenylsilyllithium greater than 50%, perhaps, one might assume that in addition to obtaining the silyllithium compound from tetraphenylsilane, some possibly arises from a direct cleavage of the silicon-hydrogen bond. The marked differences in behavior and specificity of the two types of bonds toward other chemical reagents should enable one to rationalize that the cleavage of triphenylsilane by lithium would involve one but not both types of bonds. The cleavage of diphenylsilane by sodium-potassium alloy in diethyl ether and by lithium in tetrahydrofuran tends to support a rationalization based on the scission of a silicon-phenyl linkage rather than a silicon-hydrogen bond. The cleavage of two biphenyl groups from

tri-2-biphenylsilane should not be misconstrued to imply that a silicon-hydrogen bond cannot be cleaved since, in this case, the bond is shielded by the bulky 2-biphenyl groups. It does indicate, however, that it is possible for more than one aryl group in a triarylsilane to be cleaved by lithium in tetrahydrofuran.

If the silicon-hydrogen bond is not attacked by lithium, one might envisage triphenylsilyllithium as being formed by either of two reaction paths. Firstly, the triphenylsilyllithium might be assumed to originate exclusively via tetraphenylsilane. Secondly, in addition to obtaining triphenylsilyllithium by way of tetraphenylsilane, one might consider a reaction in which phenyllithium reacts with a species, $(C_6H_5)_2SiLiH$, which could be derived from the cleavage of

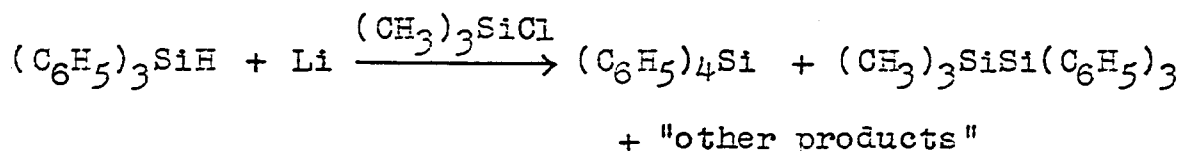


triphenylsilane by lithium. The second route involves a reaction which is definitely unattractive since it requires a nucleophile to approach a silicon atom with a high electron density. It is not entirely improbable, however, in view of a reaction in which triphenylsilanol was treated with *n*-butyllithium to give *n*-butyldiphenylsilanol⁷⁹. The evidence

⁷⁹H. Gilman, R. A. Benkeser, and G. E. Dunn, J. Am. Chem. Soc., **72**, 1689 (1950).

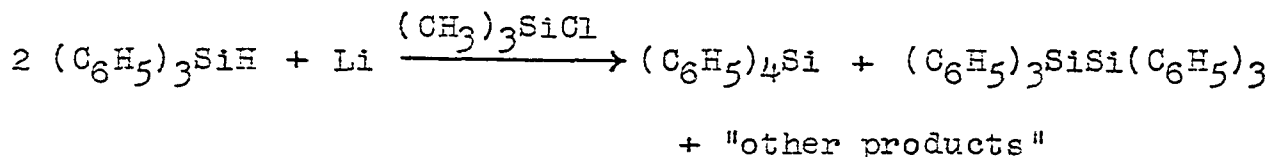
on hand is ambiguous and does not permit one to distinguish between the two paths. This ambiguity is due, in part, to an inability to detect or isolate any silicon-containing species other than triphenylsilyllithium.

Apropos the first reaction path, the experimental data do not rigorously establish the mode of formation of tetraphenylsilane. From the reaction in which the molar ratio of triphenylsilane to lithium was approximately 1:1 and in which both tetraphenylsilane and triphenylsilyllithium were detected,



one might infer that tetraphenylsilane is not only formed from uncleaved triphenylsilane and phenyllithium derived from triphenylsilane, but some may also originate from uncleaved triphenylsilane and phenyllithium derived from tetraphenylsilane. In partial support of the latter view, tetraphenylsilane was cleaved smoothly by lithium in tetrahydrofuran to give 1,1,1-trimethyl-2,2,2-triphenyldisilane and trimethylphenylsilane, subsequent to treatment of the reaction mixture with trimethylchlorosilane.

The reaction in which the molar ratio of triphenylsilane to lithium was approximately 2:1 is of particular interest. At a first glance this reaction seemed to be



reminiscent of a reported one in which triphenylsilyllithium was allowed to react with triphenylsilane in ethylene glycol dimethyl ether for 4 days at room temperature. The products consisted of a small amount of tetraphenylsilane, considerable hexaphenyldisilane, and some recovered starting material. No explanation was offered for this reaction. In the same publication it was observed, by contrast, that triphenylsilylpotassium reacted with triphenylsilane in diethyl ether to give primarily tetraphenylsilane⁸⁰.

The reaction of triphenylsilyllithium with triphenylsilane (2:1 molar ratio of triphenylsilane to triphenylsilyllithium) was run in tetrahydrofuran under conditions similar to those used for the cleavage reaction. Under these conditions and subsequent to treatment of the reaction mixture with trimethylchlorosilane, most of the triphenylsilane was recovered unchanged, but small amounts of 1,1,1-trimethyl-2,2,2-triphenyldisilane, hexaphenyldisilane, tetraphenylsilane, and triphenylsilanol were also isolated. Most of the triphenylsilyllithium was unaccounted for. Although hexaphenyldisilane was found, the amount was so small that one cannot really attribute

⁸⁰A. G. Brook and H. Gilman, ibid., 76, 2333 (1954).

or refute the formation of hexaphenyldisilane in the cleavage reaction as being due to the reaction of triphenylsilyllithium with triphenylsilane. This problem needs to be more carefully scrutinized.

When triphenylsilyllithium and triphenylsilane were refluxed in tetrahydrofuran, a good yield of tetraphenylsilane was obtained. Thus, this reaction is very similar to the one wherein tetraphenylsilane was formed from triphenylsilylpotassium and triphenylsilane in diethyl ether.

In an effort to throw more light on the cleavage of triphenylsilane by lithium, an indirect approach was taken involving triphenylgermane. Gilman and Gerow⁸¹ found that triphenylgermane was metalated by *n*-butyllithium to give triphenylgermyllithium in a very good yield. Repetition of this reaction in tetrahydrofuran using phenyllithium prepared in diethyl ether yielded, subsequent to treatment of the reaction mixture with *n*-octadecyl bromide, 80% of *n*-octadecyltriphenylgermane; thus, indicating that the reaction proceeds in the same manner and with at least equal facility in tetrahydrofuran. In view of this finding, it was thought that the cleavage of triphenylgermane by lithium should yield a maximum of 50% of triphenylgermyllithium unless more than one phenyl group was being cleaved from one molecule of triphenylgermane.

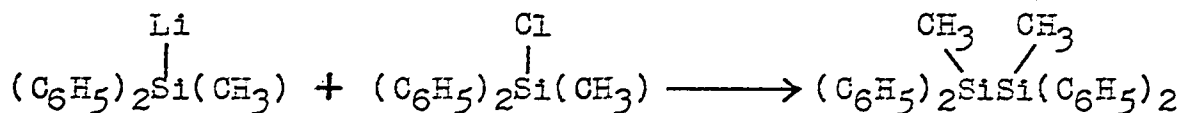
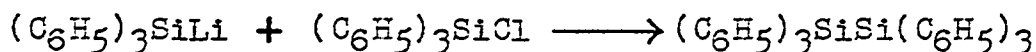
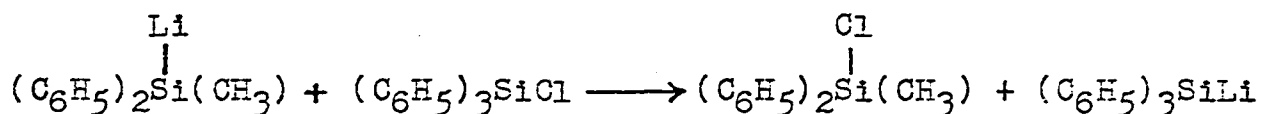
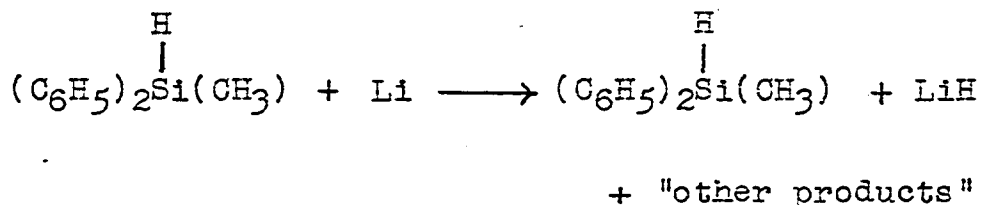
⁸¹H. Gilman and C. W. Gerow, *ibid.*, 78, 5435 (1956).

In the two runs made, the yield of triphenylgermyllithium, isolated as n-octadecyltriphenylgermane, did not exceed 50%. However, the fate of the cleaved germanium-containing segment was never conclusively determined. In one run, distillation of the residue, after removal of n-octadecyltriphenylgermane, yielded a fraction boiling at 215° at 0.005 mm. Infrared analysis of this fraction showed bands characteristic of an aromatic carbon-hydrogen bond (3.3μ), a methylene carbon-hydrogen bond (3.4μ , 3.5μ), a germanium-hydrogen bond (4.95μ), and a phenyl-germanium linkage (9.1μ). An unsuccessful attempt was made to convert this material to di-n-octadecyldiphenylgermane by successively treating it with n-butyllithium and n-octadecyl bromide.

These cleavage studies were also extended to include methyldiphenylsilane. In this case, the cleavage mixture, when treated with triphenylchlorosilane, yielded a variety of products, depending on the order of addition of the reactants. When triphenylchlorosilane was added to the cleavage mixture, the major product was hexaphenyldisilane, while a small amount of 1,2-dimethyl-1,1,2,2-tetraphenyldisilane was also found. The yield of the latter compound was uncertain because of the difficulty in working up the reaction mixture.

These products can best be accounted for by assuming the first step in the reaction involves a halogen-metal interconversion between methyldiphenylsilyllithium, which is one of the

products from the cleavage of methyldiphenylsilane by lithium, and triphenylchlorosilane. Then, coupling reactions between the various R_3SiLi and the R_3SiCl compounds could occur to give the observed products. The sequence of reactions is illustrated below.



The yields of products indicate that, at least in this reaction, triphenylsilyllithium shows a definite preference to couple with triphenylchlorosilane and very little, if any, tendency to couple with methyldiphenylchlorosilane. On the other hand, methyldiphenylsilyllithium shows a marked tendency to participate in a halogen-metal interconversion reaction. It is conceivable that the unsymmetrical coupling product, methylpentaphenyldisilane, was present in the reaction mixture,

but difficulties in working up the mixture did not permit its isolation.

That a halogen-metal interconversion occurred and, moreover, that lithium hydride was present in the reaction mixture was shown in a reaction which differed from the one just described only by the fact that the cleavage mixture was added to triphenylchlorosilane. Again, in this case, hexaphenyldisilane was the main product, but this was the only isolable compound common to both runs. The other products were methyldiphenylsilane and triphenylsilane. The formation of these products can be explained by once again visualizing a reaction in which triphenylsilyllithium, which is formed via a halogen-metal interconversion reaction, couples preferentially with triphenylchlorosilane. Since the concentration of methyldiphenylchlorosilane formed during the halogen-metal interconversion reaction is very small in comparison to the concentration of triphenylchlorosilane, and since methyldiphenylsilyllithium preferentially undergoes an interconversion reaction with triphenylchlorosilane, it is not surprising that hexaphenyldisilane was the only coupling product which was isolated. Thus, since the only coupling product is hexaphenyldisilane, the triphenylchlorosilane not utilized in the halogen-metal interconversion or in the coupling reaction, together with methyldiphenylchlorosilane formed via the halogen-metal

interconversion, are susceptible to reduction by lithium hydride.

Incidental to the cleavage studies, the stability of triphenylsilyllithium in tetrahydrofuran was briefly studied. Although triphenylsilyllithium is stable in tetrahydrofuran at room temperature, it apparently reacts with the solvent during refluxing to give a compound which has been tentatively identified as 4-hydroxybutyltriphenylsilane on the basis of elemental analysis and infrared analysis. No other pure compound was isolated from the reaction mixture.

Cyclic Organosilicon Compounds

After surveying numerous organosilicon compounds for the purpose of determining the effects of various organic groupings on the physical properties of organosilicon compounds, it was decided to begin searching for a functional nucleus in which some of the more promising organic radicals could be incorporated. The nucleus selected for this investigation was a silicon analog of fluorene. This nucleus will be referred to as dibenzosilole throughout the remaining discussion.

The first dibenzosilole compound was synthesized by treating 2,2'-biphenylenedilithium with diphenyldichlorosilane to give a low yield of 5,5-diphenyldibenzosilole and an unidentified material which was thought originally, on the basis

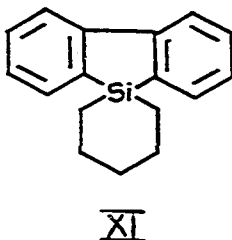
of the analytical data, to be bis-(2-biphenyl)-diphenylsilane. However, comparison of its melting point and infrared spectrum with an authentic sample prepared by a less ambiguous method showed the two to be different⁵².

Before synthesizing any more dibenzosilole compounds, it was deemed necessary to find the best method to prepare the intermediate 2,2'-biphenylenedilithium from 2,2'-dibromobiphenyl. Previously, preparation via a halogen-metal interconversion reaction, i.e., reaction of 2,2'-dibromobiphenyl with *n*-butyllithium, gave 81% of the benzophenone adduct⁵². In view of the excellent yield of the organodilithium compound obtained by Wittig and Herwig⁸² from 2,2'-diiodobiphenyl and lithium metal in diethyl ether, the same method was tried with 2,2'-dibromobiphenyl. As the yield of the benzophenone adduct was only 46%, it appears that the method of choice, when using 2,2'-dibromobiphenyl, is one involving the halogen-metal interconversion reaction.

With a good method available for obtaining 2,2'-biphenylenedilithium, procedures for the synthesis of dibenzosilole compounds were thoroughly investigated and broadened to include both functional and nonfunctional types. When di-*n*-dodecyldichlorosilane and diethyldichlorosilane were treated with 2,2'-biphenylenedilithium, poor yields of 5,5-di-*n*-dodecyl- and

⁸²G. Wittig and W. Herwig, Ber., 87, 1511 (1954).

5,5-diethyldibenzosilole were obtained. Likewise, a very poor yield of spiro-[dibenzosilole-5,1'-silacyclohexane] (XI) was

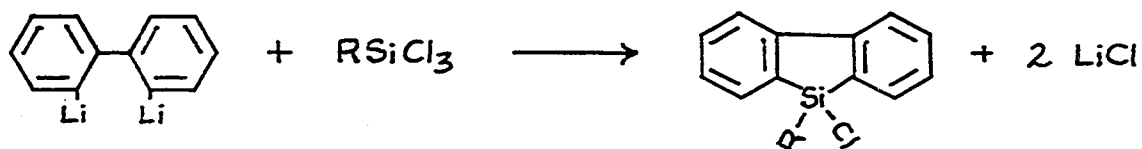


obtained when 1,1-dichlorosilacyclohexane was allowed to react with 2,2'-biphenylenedilithium. Also, a small amount of 1,1-bis-(2-biphenyl)-silacyclohexane was isolated from the same reaction mixture.

These low yields were not too surprising inasmuch as West⁸ observed that in preparing alicyclic organosilicon compounds by a cyclization reaction the yield of cyclic product increased as the number of chlorine atoms attached to silicon was increased. He attributed this to the fact that the additional chlorine atoms set up a stronger electrostatic field which facilitated the ring closure reaction. In other words, the higher polarity of a silicon-chlorine bond as compared to a carbon-silicon bond renders the silicon atom more susceptible to attack by nucleophilic reagents. One might suspect, therefore, that functional dibenzosilole compounds, i.e., compounds

containing a carbon-chlorine bond, should be obtained in higher yields than nonfunctional types. Indeed, this was found to be true but for one exception which can be readily explained.

Methyl-, *n*-dodecyl-, and phenyltrichlorosilane all coupled with 2,2'-biphenylenedilithium to give excellent yields of 5-chloro-5-methyl-, 5-chloro-5-*n*-dodecyl-, and 5-chloro-5-phenyldibenzosilole, respectively, in addition to small but varying amounts of 5,5'-spirobi-[dibenzosilole]. Only the



n-dodecyl and phenyl derivatives were analytically pure. The latter was obtained in a pure state and in a good yield only when refluxing was applied during the addition of the organo-dilithium compound to phenyltrichlorosilane. The main impurity in 5-chloro-5-methyldibenzosilole appeared to be biphenyl.

In order to minimize the formation of the spiro organo-silicon compound, it was essential to use a large excess of alkyl- or aryltrichlorosilane. Another factor influencing the yield was the concentrations of reactants, i.e., the yield of spiro compound increased with increased concentrations of reactants.

A mediocre yield of 5,5-dichlorodibenzosilole, which was not analytically pure, was obtained by the ring closure method. The low yield is not difficult to explain since an appreciable amount of 5,5'-spirobi-[dibenzosilole] was isolated even when a large excess of silicon tetrachloride was employed. The spiro organosilicon compound was prepared in a good yield from two moles of 2,2'-biphenylenedilithium and one mole of silicon tetrachloride. The germanium analog, 5,5'-spirobi-[dibenzo-germole], was prepared in essentially the same manner but in a lower yield.

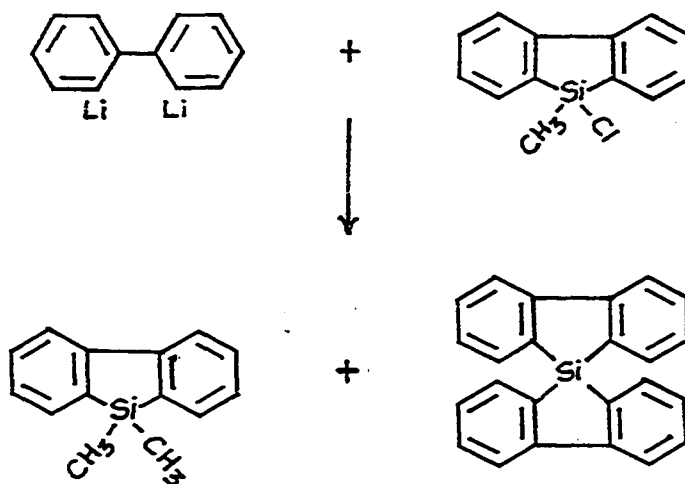
The formation of small quantities of 5,5'-spirobi-[dibenzosilole], in addition to the desired chloro substituted dibenzosilole, is indeed surprising, since this implies that an alkyl or aryl group attached to the 5-position is being displaced by an organolithium compound. In the case of non-cyclic organosilicon compounds, it has been found that tetraaryl- and arylalkylsilanes are unaffected by *n*-butyllithium in diethyl ether⁸³. Benzyltriphenylsilane is an exception, but even in this case it has been demonstrated that the cleavage occurs during work-up of the reaction mixture⁸⁴.

In order to elucidate the reaction path, 5-chloro-5-methyldibenzosilole was treated with an equimolar quantity of

⁸³H. Gilman, R. A. Benkeser, and G. E. Dunn, J. Am. Chem. Soc., **72**, 1689 (1950).

⁸⁴H. Gilman and H. Hartzfeld, ibid., **73**, 5878 (1951).

2,2'-biphenylenedilithium in diethyl ether to yield almost equimolar amounts of 5,5'-spirobi-[dibenzosilole] and 5,5-dimethyldibenzosilole. The latter was synthesized unambiguously from 5-chloro-5-methyldibenzosilole and methyllithium.



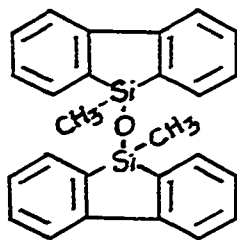
Thus, it appears 2,2'-biphenylenedilithium first displaces the chlorine atom; then, the methyl-silicon linkage is cleaved simultaneously or in a very rapid step-wise fashion by the second anion to yield the spiro organosilicon compound and methyllithium which, in turn, can couple with unreacted 5-chloro-5-methyldibenzosilole to give the dimethyl derivative. The fact that approximately equimolar amounts of products were obtained strongly supports a concerted or very rapid coupling-cleavage type of reaction. The only other conceivable way by

which one can visualize the origin of these products is to assume that the 5-chloro-5-methyldibenzosilole contained considerable amounts of 5,5-dichloro- and 5,5-dimethyldibenzosilole. There was no evidence for either of these being present in the starting material. That the reaction seems to be intimately related to the formation of the spiro compound is illustrated by the failure of 2,2'-biphenylenedilithium to react in a similar fashion with triethylchlorosilane to give 5,5-diethyldibenzosilole.

Several symmetrically and unsymmetrically substituted dibenzosilole derivatives were synthesized in excellent yields from a 5-alkyl-5-chlorodibenzosilole and an organolithium compound. 5-n-Dodecyl-5-phenyldibenzosilole, 5-(3-biphenyl)-5-n-dodecyldibenzosilole, [(methyldibenzylsilyl)-methyl]-5-n-dodecyldibenzosilole, and 5-n-dodecyl-5-n-hexadecyldibenzosilole were prepared in good yields from 5-chloro-5-n-dodecyldibenzosilole and the respective organolithium compounds. An isomer of the last compound, 5,5-di-n-tetradecyldibenzosilole, was obtained from the reaction of 5,5-dichlorodibenzosilole with n-tetradecyllithium. This procedure is not only an excellent method for obtaining unsymmetrical, high molecular weight molecules, but it is also the method of choice for preparing symmetrically substituted types.

It may be recalled that, originally, 5,5-diphenyldibenzosilole was prepared in a low yield from diphenyldichlorosilane and 2,2'-biphenylenedilithium⁵². To more clearly establish the structure of this compound, as well as to find a better method of preparation, it was synthesized from three different dibenzosilole compounds. Thus, 5-phenyldibenzosilole, 5-chloro-5-phenyldibenzosilole, and 5,5-dichlorodibenzosilole, when treated with phenyllithium, all gave the diphenyl derivative in yields exceeding 70%. This not only gives firmer support to the structure of the compound, but it again reflects the superiority of the two-step method over a one-step method for preparing symmetrically substituted dibenzosilole types.

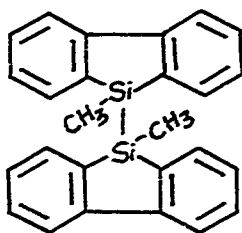
Hydrolysis reactions of compounds of the type 5-alkyl-5-chlorodibenzosilole proceeded in an expected manner. Neutralization of 5-chloro-5-methyldibenzosilole with sodium hydroxide afforded either 5-hydroxy-5-methyldibenzosilole or 5,5'-oxybis-[5-methyldibenzosilole] (XII), depending on conditions used in



XII

working up the reaction mixture. Hydrolysis of 5-chloro-5-n-dodecyldibenzosilole with either sodium hydroxide or water gave only 5,5'-oxybis-[5-n-dodecyldibenzosilole]. The structure of 5-hydroxy-5-methyldibenzosilole is uncertain at the present time as the analysis indicated the compound to be the disiloxane; however, its melting point was different from that of the disiloxane compound and, also, the infrared spectrum showed a strong absorption band indicative of a Si-OH bond (2.7μ) but no band characteristic of a Si-O-Si linkage (9.5μ).

Two dibenzosilole compounds containing a silicon-silicon bond were prepared for use in some subsequent cleavage studies. Both 5,5'-dimethyl-5,5'-bi-[dibenzosilole] (XIII) and 5,5'-di-n-dodecyl-5,5'-bi-[dibenzosilole] were prepared by sodium condensations from the respective 5-alkyl-5-chlorodibenzo-siloles. In surprising contrast, a similar coupling reaction



XIII

between sodium and 5-chloro-5-phenyldibenzosilole gave only what tentatively appears to be 5,5'-oxybis-[5-phenyldibenzosilole], subsequent to hydrolysis of the reaction mixture.

Another approach to the synthesis of dibenzosilole compounds containing a silicon-silicon bond was one in which one mole of hexachlorodisilane was treated with two moles of 2,2'-biphenylenedilithium. 5,5'-Spirobi-[dibenzosilole] was the only organosilicon compound isolated from the reaction mixture. A considerable amount of what appeared to be mainly a silicon-containing inorganic material was also found. This was insoluble in all of the common organic solvents.

In all likelihood, the expected coupling product, 5,5'-dichloro-5,5'-bi-[dibenzosilole], was formed to some extent as an intermediate, but this compound, or even possibly 5-chloro-5-trichlorosilyldibenzosilole, can be attacked further by 2,2'-biphenylenedilithium by displacing a chlorine atom to form a carbon-silicon bond, subsequent to a rapid or simultaneous cleavage of the silicon-silicon bond by the second anion of the organodilithium compound. This reaction resembles that of 5-chloro-5-methyldibenzosilole with 2,2'-biphenylenedilithium except for one notable difference. In one case, a carbon-silicon bond is cleaved, while in the other a silicon-silicon bond is ruptured. It has been well-established that a silicon-silicon bond can be cleaved when treated with certain arylating and alkylating reagents, e.g., when octachlorotrisilane was treated with phenylmagnesium bromide, a mixture of tetraphenylsilane and hexaphenyldisilane was obtained. Even the treatment

of halogenated disilane compounds with zinc alkyls, Grignard reagents, and metallic sodium resulted in some scission of the single silicon-silicon bond⁸⁵. One might expect, therefore, that after one of the carbon-lithium bonds of 2,2'-biphenylenedilithium interacts with the silicon-chlorine bond of the dibenzosilole compound, the scission of the silicon-silicon bond by the second anion would be more facile than cleavage of a carbon-silicon bond.

Some compounds containing the dibenzosilole nucleus were reactive toward both acidic and basic reagents. 5,5-Diphenyldibenzosilole was cleaved by formic acid to give biphenyl and an impure silicon-containing fragment. This reaction is reminiscent of similar cleavages of 2-biphenyllyl substituted organosilicon compounds by formic acid⁸⁶.

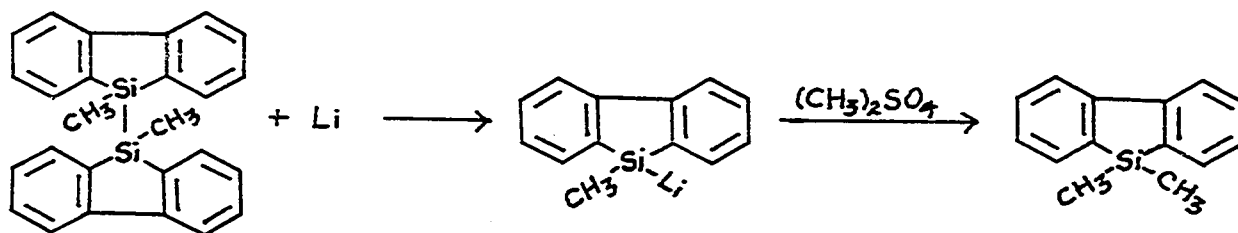
A noteworthy and somewhat unexpected reaction was one wherein 5,5'-spirobi-[dibenzosilole] was attacked by phenyllithium in tetrahydrofuran to give 5-(2-biphenyllyl)-5-phenyldibenzosilole, a compound which was synthesized unambiguously from 2-biphenyllyllithium and 5-chloro-5-phenyldibenzosilole. The reaction was unexpected in that it is essentially a reversal of the one in which the spiro compound was formed from 2,2'-biphenylenedilithium and 5-chloro-5-methyldibenzosilole. A more careful examination of both reactions reveals that in the reaction in which the spiro compound was formed, the

⁸⁵E. G. Rochow, "An Introduction to the Chemistry of the Silicones," John Wiley and Sons, Inc., New York, N. Y., 1951, p. 61.

⁸⁶H. Gilman and K. Oita, J. Am. Chem. Soc., **77**, 3386 (1955).

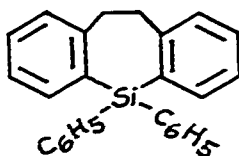
methyllithium arising from the scission of the methyl-silicon linkage can interact with more 5-chloro-5-methyldibenzosilole. On the other hand, in the reaction of 5,5'-spirobi-[dibenzosilole] with phenyllithium, no silicon-chlorine bond is available for the possible intermediate 5-(2'-lithio-2-biphenyl)-5-phenyldibenzosilole to react with after one of the rings in the spiro compound has been opened. Since Color Test I⁴⁰ was negative before hydrolysis of the reaction mixture, this might imply that the carbon-lithium bond is destroyed in some fashion, possibly by interaction with solvent. It is also conceivable that the organolithium compound formed after ring opening does not react with Michler's ketone because of steric hindrance. In any event, the reaction requires a closer examination before any conclusion can be reached in regard to a possible mechanism.

The good yield of triphenylsilyllithium obtained from hexaphenyldisilane and lithium in tetrahydrofuran was the impetus for a similar study with a dibenzosilole compound containing a silicon-silicon bond. Treatment of 5,5'-dimethyl-5,5'-bi-[dibenzosilole] with an excess of lithium in tetrahydrofuran gave 5-lithio-5-methyldibenzosilole which, when allowed to react with dimethyl sulfate, afforded 5,5-dimethyldibenzosilole. This type of cleavage reaction has potential of being an excellent method for obtaining intermediates of synthetic utility.



Interestingly enough, 5,5-dimethyldibenzosilole was not cleaved by lithium, but rather seemed to absorb the lithium in some fashion.

Another type of cyclic organosilicon compound briefly examined was one formed from 2,2'-dilithiobibenzyl and diphenyldichlorosilane. The product, which was obtained in a very low yield, was 10,11-dihydro-5,5-diphenyldibenzosilepin (XIV). Further studies on this nucleus were not pursued because the synthesis of functional types did not appear promising.



XIV

In Table 5, the thermal stability data for the dibenzosilole compounds which have been screened are given. Three of the compounds, which are liquids at room temperature, appear to be of particular promise, especially since they volatilize at approximately 450° with little decomposition. These are 5-n-dodecyl-5-n-hexadecyldibenzosilole, 5,5-di-n-tetradecyldibenzosilole, and 5-n-dodecyl-5-[(methyldibenzylsilyl)-methyl]-dibenzosilole.

All of the infrared spectra of dibenzosilole compounds in carbon disulfide or in carbon tetrachloride or as liquids showed an absorption band at 8.9μ . The 5,5-diaryldibenzosiloles exhibited a split band at 9.4μ as did 5,5'-dialkyl-5,5'-bi-[dibenzosilole] types. The 5-alkyl-5-aryldibenzosiloles had sharp bands at 9.3μ and 9.4μ , while the 5,5-dialkyldibenzosiloles had only the band at 9.4μ . It appears, therefore, that the dibenzosilole nucleus can be identified by the bands at 8.9μ and 9.4μ , providing at least one aryl or alkyl group is attached to the 5-position. The absorption bands characteristic of a Si-OH bond, a Si-H bond, and a Si-O-Si linkage appeared at 2.7μ , 4.85μ , and 9.5μ , respectively, in the spectra of dibenzosilole compounds containing these bonds.

Table 5. Thermal stabilities of aromatic cyclic organosilicon compounds^a

Compound	M.p., °C	Thermal stability, °C
Spiro-5,5'-bi-[dibenzo-silole]	226-228	vol. 460-470
Spiro-5,5'-bi-[dibenzo-germole]	245-246	vol. 470-480
5,5-Diphenyldibenzosilole	148-149	vol. 440-450
5,5-Dimethyldibenzosilole	59-60	vol. 290-295
5,5-Diethyldibenzosilole	60-61	vol. 315-320
5,5-Di- <u>n</u> -dodecyl-dibenzosilole	240/0.008 ^b	vol. 420-430 (lt. brn.)
5,5-Di- <u>n</u> -tetradecyl-dibenzosilole	248/0.005 ^b	vol. 440-450
Spiro-[dibenzosilole-5,1'-silacyclohexane]	145-146	vol. 390-395
5- <u>n</u> -Dodecyl-5- <u>n</u> -hexadecyldibenzosilole	235/0.005 ^b	vol. 460
5- <u>n</u> -Dodecyl-5-phenyl-dibenzosilole	198/0.012 ^b	vol. 410-420
5-(3-Biphenyl)-5- <u>n</u> -dodecyldibenzosilole	247/0.008 ^b	vol. 430-440
5- <u>n</u> -Dodecyl-5-[(methyl-dibenzylsilyl)-methyl]-dibenzosilole	250/0.005 ^b	vol. 460-470
5-Benzoyldibenzosilole	69-70	vol. 400-410

^aOne organogermanium compound is included.^bB.p., °C/mm.

Table 5. (Continued)

Compound	M.p., °C	Thermal stability, °C
5,5'-Dimethyl-5,5'-bi-[dibenzosilole]	185-186	vol. 460
5,5'-Di-n-dodecyl-5,5'-bi-[dibenzosilole]	59-61	vol. 470-480 (lt. brn.)
5,5'-Oxybis-[5-methyl-dibenzosilole]	127-128	vol. 450-460
5,5'-Oxybis-[5-n-dodecyl-dibenzosilole]	74-75	vol. 470-480 (lt. brn.)
10,11-Dihydro-5,5-diphenyldibenzosilepin	173-174	vol. 420; orange residue 450

Suggestions for Further Research

The reaction of fluorene, 9-phenylfluorene, and triphenylmethane with lithium in liquid ammonia should be investigated in order to determine the importance of solvent on this type of reaction.

It would be worthwhile to extend the cleavage reactions of compounds containing a silicon-hydrogen bond to phenylsilane. Also, attention might be directed toward a possible method or methods to differentiate between the possible reaction paths. In this respect, the triphenylgermane cleavage

could be examined more carefully. In connection with these cleavages, the reaction of triphenylsilyllithium with triphenylsilane at room temperature and at reflux temperature needs to be examined more thoroughly in order to elucidate the reaction paths. The reaction at room temperature might yield more fruitful results if allowed to proceed for a week or longer.

The structure of 4-hydroxybutyltriphenylsilane should be more rigorously established. One method by which this might be accomplished would be to convert the alcohol to the chloride with thionyl chloride and then prepare the Grignard reagent, which would give n-butyltriphenylsilane subsequent to hydrolysis with water.

For the purpose of gaining thermally stable compounds, it might be profitable to prepare more unsymmetrically substituted dibenzosilole compounds by utilizing some of the organic groupings found promising in this laboratory.

The synthetic utility of 5-chloro-5-methyldibenzosilole should be determined more fully and extended to other compounds of this type. The mode of addition of lithium to 5,5-dimethyldibenzosilole might be established by treating the lithium adduct, or more likely the dilithium adduct, with dimethyl sulfate.

SUMMARY

A literature survey of all cyclic organosilicon compounds prepared prior to April, 1957 has been made.

In searching for compounds with good thermal stabilities, as well as wide liquid ranges, several organosilicon compounds have been screened for the purpose of comparing the effectiveness of various organic radicals in contributing to either or both of these properties. Emphasis was placed on the m-halophenyl and R_3SiCH_2- groupings. In addition, some organic radicals found to be promising by others were incorporated into organosilicon compounds having $R_3SiCH_2CH_2SiR_3$ and $R_3SiC_6H_4SiR_3$ skeletons.

Tetrahydrofuran has been found to be a solvent of choice for the metalation of heterocyclic compounds by an organolithium compound. It also has been found to be an excellent solvent for the reaction of certain hydrocarbons like cyclopentadiene and fluorene with lithium metal. The cleavage of a phenyl-carbon linkage in 9,9-diphenylfluorene is facilitated in tetrahydrofuran.

Organosilicon compounds containing a silicon-hydrogen bond have been cleaved by lithium metal in tetrahydrofuran. Thus, diphenylsilane gave triphenylsilane; tris-2-biphenylsilane yielded 2-biphenyllithium; triphenylsilane afforded triphenylsilyllithium; methyldiphenylsilane yielded methyldiphenylsilyl-

lithium. Tetraphenylsilane has been shown to be an intermediate in the cleavage reaction of triphenylsilane by lithium.

In order to have a nucleus which could lead to thermally stable organosilicon compounds, as well as provide functional intermediates to be utilized for the synthesis of unsymmetrical nonfunctional compounds, several 5-R-5-chlorodibenzosiloles have been prepared where R is methyl, *n*-dodecyl, benzyl, and phenyl. These intermediates, when treated with appropriate organolithium compounds, have resulted in some promising liquids of high thermal stability.

Compounds of the type 5-R-5-chlorodibenzosilole have been found to hydrolyze to give either a silanol or a disiloxane, depending on the work-up conditions and on the kind of R group. They have been reduced by lithium aluminum hydride and generally can be condensed by sodium to give a disilane compound. An exception was 5-chloro-5-phenyldibenzosilole. In this case, the disiloxane compound was isolated subsequent to hydrolysis of the reaction mixture.

The following reactions were those in which carbon-silicon bonds and in one case a silicon-silicon bond were attacked by an organolithium compound: reaction of 2,2'-biphenylenedilithium with 5-chloro-5-methyldibenzosilole gave 5,5'-spirobi-[dibenzosilole]; reaction of 2,2'-biphenylenedilithium with hexachlorodisilane yielded the spiro compound; reaction of phenyllithium with the spiro organosilicon compound afforded

5-(2-biphenylyl)-5-phenyldibenzosilole. The last compound was synthesized unambiguously from 5-chloro-5-phenyldibenzosilole and 2-biphenylyllithium.

5,5'-Dimethyl-5,5'-bi-[dibenzosilole] has been cleaved by lithium in tetrahydrofuran to give 5-lithio-5-methyldibenzosilole which has potential as a synthetic intermediate. 5,5-Dimethyldibenzosilole, by contrast, was not cleaved by lithium, but rather appeared to absorb the metal in some fashion.

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